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HOMOGENEOUS CONSTITUTIVE EQUATIONS FOR MATERIALS WITH PERMANENT MEMORY

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LIST OF SYMBOLS

Symbol	Definition
$A[\theta]$	Temperature Shift Function
$A_{ijk\ell}$	Strain Coefficient
a	Scalar
b	Scalar
$C_{ijk\ell}$	Kernel Function
d	Displacement
$D(t)$	Linear Damage Function
$D'(t)$	Nonlinear Damage Function
$\underline{e}$	Cauchy Infinitesimal Strain Tensor
e_{ij}	Components of Cauchy Strain Tensor
$e_{ij}(\tau)_{0}^{t}$	History of Components of Cauchy Strain Tensor
e	Uniaxial Applied Strain
e_i	Local Uniaxial Strain in i^{th} Element
e_{max}	Local Failure Strain
$\underline{E}$	Green Strain Tensor

E_{ij}		Components of Green Strain Tensor
$E_{ij}\overset{t}{\underset{o}{(\tau)}}$		History of Components of Green Strain Tensor
f		Function
$f\overset{t}{\underset{o}{(\xi)}}$		History of Function
$\underline{F}$		Deformation Gradient Tensor
F_{ij}		Components of Deformation Gradient Tensor
$I_i(t)$	=	Current Value of i^{th} Strain Invariant
I_i°	=	Value of i^{th} Strain Invariant at the Reference Time
$I_i\overset{t}{\underset{o}{(\xi)}}$	=	History of i^{th} Strain Invariant
$J_i(t)$		Current Value of i^{th} Stress Invariant
J_i°		Value of i^{th} Stress Invariant at the Reference Time
$J_i\overset{t}{\underset{o}{(\xi)}}$		History of i^{th} Stress Invariant
$k_{ij}\cdot\cdot p_n q_n$		Kernel Functions
L_i		Kernel Functions
$N(\tau)$		Distribution of Strain Intensity Factors
p		Integer
P		Pressure
q		Integer
r		Integer, radius

$\underline{S}$	Stress Tensor
S_{ij}	Components of Stress Tensor
t	Current Time
t'	Current Value of Reduced Time
t_k	Time Held at k^{th} State
t_{fk}	Time to Failure for k^{th} State
T	Time, Limit of Memory
u_i	Components of Displacement Vector
x_i	Cartesian Coordinates
x_i'	Reference Configuration
γ	Relaxation Time
δ_{ij}	Kronecker Delta Function
ξ	Dummy Time
ξ'	Reduced Dummy Time
θ	Temperature
μ	Poisson's Ratio
ν_j	Direction Cosines
ρ	Radius
τ	Dummy Time, Strain Intensity Factor
τ'	Reduced Dummy Time
∇^2	Laplacian Operator
$\lvert\cdot\rvert$	Absolute Value
$\lvert\lvert\cdot\rvert\rvert$	Maximum Absolute Value in Past History
$\lvert\lvert\cdot\rvert\rvert_\infty$	Maximum Absolute Value in Past History

$\|\cdot\|_p$	L^p Norms
$\|\cdot\|_{h,p}$	Weighted L^p Norms
$\|\cdot\|_{h,p}^r$	Weighted L^p Norms With Respect to a Reduced Time
F	Functional
G	Functional
H	Functional
J	Functional
L	Functional
M	Functional
N	Functional
P	Functional

ABSTRACT

Non-linear homogeneous constitutive equations are developed in this thesis for highly filled polymeric materials such as solid propellants. In the range of strains below vacuole dilatation these materials obey the homogeneity rule of linearity but do not obey the superposition rule. Such materials typically exhibit an irreversible "stress softening" called the "Mullins Effect."

The development in this dissertation stems from attempting to mathematically describe the failing microstructure of these composite materials in terms of a linear cumulative damage model. It is demonstrated that p^{th} order Lebesgue norms of the strain history can be used to describe the state of damage in these materials and can also be used in the constitutive equation to characterize their time dependent mechanical response to strain disturbances.

Stress analysis procedures for materials having non-linear homogeneous constitutive equations are developed for two and three dimensional proportional boundary value problems. A series of correspondence principles are derived wherein half of the solution, either the stresses or the strains, can be obtained by solving an equivalent linear elastic problem. The remaining half of the solution can be obtained by substituting the linear elastic solution into the non-linear homogeneous constitutive equation.

The constitutive equation has been extended to include thermo-rheologically simple materials by defining a reduced time. It is

also demonstrated that by using weighted p^{th} order Lebesgue norms the constitutive equation can also contain the rehealing of damage which is exhibited by highly filled polymeric materials.

I.0 INTRODUCTION

This thesis deals with non-linear homogeneous constitutive equations of degree one, a type of behavior that until now has not been mentioned in the field of mechanics. This type of behavior satisfies one of the two requirements for linearity and in the author's opinion constitutes the simplest type of non-linear behavior. Because one of the linearity requirements is satisfied by these materials, they are often mistaken for linear materials [1], since the characterization procedures used by many laboratories do not differentiate between linear and homogeneous behavior [2]. The difficulty lies in differentiating between necessary conditions and sufficient conditions to guarantee linear behavior. If a material is linear, it will always have a homogeneous constitutive equation. However, if a material has a homogeneous constitutive of degree one, it need not be linear.

The existence of materials having a homogeneous but non-linear constitutive equation was first discussed in the author's Master's Thesis, "Applications of Viscoelasticity to Filled Materials" [2]. In that thesis the problems of applying the linearity conditions to material characterization procedures were discussed as was the reason filled polymeric materials exhibit this type of behavior. That thesis also demonstrated that if meaningful stress analysis were to be performed on propellant structures, accurate constitutive equations for these materials must be developed.

Composite solid propellants and other highly filled polymeric materials which exhibit "stress softening" [2-8] at strains below detectable dewetting [6,9,10,11] appear to obey non-linear homogeneous constitutive equations of degree one. The stress analysis of composite propellant structures has received considerable attention in the past decade [12-18] because grain failure generally leads to missile failure. In the range of strain below detectable dewetting these propellant materials have usually been treated and thought of as linear viscoelastic solids since they have relaxation moduli that are generally independent of strain magnitude [1,2,19]. Examination of the mathematical requirement for linearity indicates that the above criterion is simply a check on the homogeneity of the constitutive equation and does not guarantee linearity.

The purpose of this thesis is, therefore, to (a) develop non-linear constitutive equations homogeneous to degree one for characterizing highly filled polymeric materials and (b) develop methods by which these constitutive equations can be used in solving two-and three-dimensional boundary valued problems.

To accomplish these goals systematically, a brief discussion of kinematic and constitutive linearity and non-linearity is introduced in Section 2. In Section 3 it is demonstrated that the existing non-linear constitutive equations for viscoelastic solids do not contain the necessary mathematical devices to describe the behavior discussed above. In Section 4 the "stress softening" or "Mullin's Effect" [2-8] is analyzed from a simple mechanical failure model of the propellant

microstructure and is seen to contain this type of non-linear behavior. Also the p^{th} order Lebesgue norms [20] of the strain history are presented as being excellent memory measures of the strain history to use in the constitutive equations.

In Section 5 the model is extended to include the general three-dimensional constitutive equation for isotropic materials. In Section 6 it is demonstrated that the use of a weighted norm [21] in the constitutive equation includes the "rehealing" of the "stress softening" which also is exhibited by these materials. Section 7 demonstrates that the extension to thermorheologically simple materials is valid.

Stress analysis procedures for materials having homogeneous constitutive equations of degree one are developed in Section 8. Here a series of correspondence principles are derived for proportional boundary value problems demonstrating that for large classes of these constitutive equations, a linear solution corresponds to half (either the stress or the strain distribution) of the actual solution. Material characterization procedures are discussed in Section 9 where one method is proposed for this type of material. In Section 10 the theory is applied to experimental data and shown to yield accurate stress predictions for a variety of strain inputs.

II. LINEARITY REQUIREMENTS

There is apparently some confusion among many practicing engineers as to what exactly constitutes a linear constitutive equation and how such a relation is obtained. In the literature on linear elasticity, linear viscoelasticity and continuum mechanics, linear constitutive laws are usually simply given and the actual mathematical requirements for linearity are never stated [22-27]. The problem is greatly complicated when considering non-linear behavior, or more precisely what condition or conditions must be violated before the material is classified as non-linear. Most non-linear theories have had their origin in the addition of second order terms to a first order equation. Is this second order theory then the simplest non-linear equation or are there even simpler non-linear forms? These questions cannot be answered until the mathematical requirements for linearity are stated, for only by violating the linearity conditions can non-linearity be defined.

When solving boundary value problems in the field of solid mechanics, non-linearities can arise in two ways, kinematic and material. Material non-linearities mean naturally a non-linear stress-strain constitutive law. Kinematic non-linearities have to do with the strain-motion relationship.

2.1 Kinematic Linearity.

Kinematic linearity has to do with motion only and has nothing to do with the force-motion relationship. The motion of a body in continuum mechanics is defined as the mapping of all points in the body from some reference configuration x_k to the deformed configuration x'_k [25,26,27]. The continuum approach interprets this motion in terms of a deformation gradient $\underline{F}$, defined by

$$F_{ij} = \partial x'_i/\partial x_j \ , \quad i,j = 1,2,3 \ . \tag{2.1}$$

Strains in continuum theory are defined in terms of the deformation gradient. There are various definitions or measures of the quantity called strain. One of the most commonly used definitions of finite strain is the Green strain tensor $\underline{E}$ defined by

$$\underline{E} = \frac{1}{2}[\underline{F}\underline{F}^T - \underline{I}] \ . \tag{2.2}$$

In the above equation $\underline{F}^T$ denotes the transpose of $\underline{F}$ and $\underline{I}$ is the unit tensor. In component form the Green strain tensor becomes

$$E_{pq} = \frac{1}{2}\left[\frac{\partial x'_i}{\partial x_p}\frac{\partial x'_i}{\partial x_q} - \delta_{pq}\right] \ , \quad \text{where } \delta_{pq} = \begin{cases} 1 & \text{if } p = q \\ 0 & \text{if } p \neq q \end{cases} \tag{2.3}$$

In texts on elasticity [22,23,24], the definition of strain is usually given in terms of the displacement gradients rather than the deformation gradients. In terms of the components u_i of the

displacement vector $\overline{u}$, which are defined by

$$u_i = x_i' - x_i,\ i = 1,2,3, \tag{2.4}$$

the Green strain tensor becomes

$$E_{pq} = \frac{1}{2}\left[\frac{\partial u_p}{\partial x_q} + \frac{\partial u_q}{\partial x_p} + \frac{\partial u_i}{\partial x_q}\frac{\partial u_i}{\partial x_p}\right] . \tag{2.5}$$

When the displacement gradients are very small, the second order terms in equation (2.5) can be ignored and the Green strain tensor reduces to the Cauchy infinitisimal strain tensor tensor e_{pq} defined by

$$e_{pq} = \frac{1}{2}\left[\frac{\partial u_p}{\partial x_q} + \frac{\partial u_q}{\partial x_p}\right] = \frac{1}{2}\left[F_{pq} + F_{qp} - 2\delta_{pq}\right] . \tag{2.6}$$

The strain-displacement gradient equation given by equation (2.6) is linear. Linear equations are defined as having one basic mathematical property which can be expressed as

$$f(a_1+x_1, a_2+x_2, \cdots) = f(a_1, a_2, \cdots) + f(x_1, x_2, \cdots) \tag{2.7}$$

In the above equation f is a function of the variables $x_1, x_2, \cdots$. If the function is linear then equation (2.7) will be satisfied for all arbitrary real scalars a_i, and all values of the variables x_i. Equation (2.7) is defined as the linearity condition for functions.

If the strains are given as linear functions of the displacement gradients $\partial u_i/\partial x_j$, the linearity condition guarantees that the strain due to several infinitesimal motions is simply the sum of the strain due to each motion acting separately. Sokolnikoff has given a mathematical proof of this superposition of strains due to several infinitesimal motions in his treatment of infinitesimal affine transformations [24]. Superposition of strain or displacements caused by infinitesimal motions is therefore justified when solving boundary value problems. Since the discussion has dealt only with motion, the superposition of infinitesimal strains for both linear and non-linear materials is justified and is independent of the linearity of the stress-strain constitutive equation and other equations entering into the problem

Since part of this dissertation attempts to show a type of correspondence between a linear solution of linear boundary valued problems and an equivalent problem wherein the stress-strain constitutive equation has a particular type of non-linearity, only the infinitesimal strain tensor e_{pq} will be used in the remainder of this dissertation. Use of this strain tensor restricts the range of valid application to cases when the displacement gradients are small.

2.2 Constitutive Linearity.

In the field of mathematics, the requirements for linearity are the same whether they be applied to differential equations, functions, operators, transforms, functionals or other mathematical operations. The linearity requirements are basically the same as those given by

equation (2.7). When these linearity requirements are applied to constitutive theories they are applied best to functional equations [28] since in continuum mechanics a simple material is defined as a material wherein the present state of stress can depend upon the history of the deformation gradients [25,26,27]. Expressed mathematically, a physically homogeneous simple material can be represented as the functional equation

$$S_{ij}(t) = G_{ij}\left[\partial x_p'(t,\tau)/\partial x_q\right]_{\tau=0}^{t} . \tag{2.8}$$

Not every relation of the form (2.8) is physically meaningful. When an arbitrary rigid rotation of the body is superimposed on a given deformation history, the stress field $\overline{S}_{ij}$ must undergo an equal rigid rotation. The form of the constitutive equation must be such that this requirement is satisfied. Green, Rivlin, and Pipkin [29-33] have shown that if the constitutive functional is expressed as

$$\overline{S}_{ij}(t) = \frac{\partial x_i'(t)}{\partial x_k} \frac{\partial x_j'(t)}{\partial x_\ell} F_{k\ell}\left[E_{pq}(t,\tau)\right]_{\tau=0}^{t} , \tag{2.9}$$

then the above mentioned restriction will be satisfied for an arbitrary time dependent rigid body rotation. In terms of the Cauchy infinitesimal strain tensor equation (2.9) becomes

$$\overline{S}_{ij}(t) = Q_{ik}(t)Q_{j\ell}(t)S_{k\ell}(t) = Q_{ik}(t)Q_{j\ell}(t)\ F_{k\ell}\left[e_{pq}(t,\tau)\right]_{\tau=0}^{t} \tag{2.10}$$

In equation (2.10) $\bar{S}_{ij}(t)$ is the stress in the rotated system, $S_{pq}(t)$ is the stress in the reference system, and $\underset{\sim}{Q}$ represents the rigid rotation of the frame of reference. With respect to the reference system the stress is given by the functional equation

$$S_{ij}(t) = F_{ij}\left[e_{pq}\overset{t}{\underset{\tau=0}{(t,\tau)}} \right] . \tag{2.11}$$

For a constitutive equation to be linear it must satisfy the following functional equation [28].

$$F_{ij}\left[ae_{pq}\overset{t}{\underset{\tau=0}{(t,\tau)}} + be'_{pq}\overset{t}{\underset{\tau=0}{(t,\tau)}} \right] = aF_{ij}\left[e_{pq}\overset{t}{\underset{\tau=0}{(t,\tau)}} \right] + bF_{ij}\left[e'_{pq}\overset{t}{\underset{\tau=0}{(t,\tau)}} \right]. \tag{2.12}$$

In equation (2.12) a and b are arbitrary scalars and e_{pq} and e'_{pq} are arbitrary strain histories. The measure of strain used in equation (2.12) can be any linear or non-linear strain-displacement gradient relationship and still yield a linear stress-strain relationship. It should be pointed out however that if a non-linear strain-displacement gradient relation is used in a linear stress-strain constitutive equation, by the time some form of strain compatibility condition is used or if the equilibrium equations are expressed in terms of the displacement gradients, the resulting system of stress-displacement gradient equations will be non-linear. It is for this reason the Cauchy strain tensor e_{pq} defined by equation (2.6) will be used in the remainder of this thesis.

2.3 Redundancy in Linearity Requirements

The linearity conditions given in equations (2.7) or (2.12) can be written as two separate rules instead of one as

$$F_{ij}\left[a e_{pq}\left(\overset{t}{\underset{\tau=0}{t,\tau}}\right)\right] = aF_{ij}\left[e_{pq}\left(\overset{t}{\underset{\tau=0}{t,\tau}}\right)\right], \text{ and} \tag{2.13a}$$

$$F_{ij}\left[e_{pq}\left(\overset{t}{\underset{\tau=0}{t,\tau}}\right) + e'_{pq}\left(\overset{t}{\underset{\tau=0}{t,\tau}}\right)\right] = F_{ij}\left[e_{pq}\left(\overset{t}{\underset{\tau=0}{t,\tau}}\right)\right] + F_{ij}\left[e'_{pq}\left(\overset{t}{\underset{\tau=0}{t,\tau}}\right)\right], \tag{2.13b}$$

where $e_{pq}(\tau)$, $e'_{pq}(\tau)$, a, are arbitrary.

Careful examination of these two conditions indicates that the first rule of linearity, called scalar multiplication or homogeneity of degree one [28,34], is contained in the second rule of linearity, called additivity or Boltzmann superposition for practical purposes. This duplication can simply be shown for all scalars that are rational numbers. The proof of this redundancy in linearity conditions can be given as follows. For all positive integers P equation (2.13b) gives

$$F_{ij}\left[P e_{pq}\left(\overset{t}{\underset{\tau=0}{t,\tau}}\right)\right] = \underbrace{F_{ij}\left[e_{pq}\left(\overset{t}{\underset{\tau=0}{t,\tau}}\right) + \ldots + e_{pq}\left(\overset{t}{\underset{\tau=0}{t,\tau}}\right)\right]}_{\text{(P times)}} =$$

$$\underbrace{F_{ij}\left[e_{pq}\left(\overset{t}{\underset{\tau=0}{t,\tau}}\right)\right] + \ldots + F_{ij}\left[e_{pq}\left(\overset{t}{\underset{\tau=0}{t,\tau}}\right)\right]}_{\text{(P times)}} = PF_{ij}\left[e_{pq}\left(\overset{t}{\underset{\tau=0}{t,\tau}}\right)\right] \tag{2.14}$$

Similarly for all positive integers Q the same equation gives

$$F_{ij}\left[e_{pq}\left(\overset{t}{\underset{\tau=0}{t,\tau}}\right)\right] = F_{ij}\left[\underbrace{\frac{1}{Q} e_{pq}\left(\overset{t}{\underset{\tau=0}{t,\tau}}\right) + \ldots + \frac{1}{Q} e_{pq}\left(\overset{t}{\underset{\tau=0}{t,\tau}}\right)}_{Q \text{ times}}\right] = \tag{2.15}$$

$$\underbrace{F_{ij}\left[\frac{1}{Q} e_{pq}\left(\overset{t}{\underset{\tau=0}{t,\tau}}\right)\right] + \ldots + F_{ij}\left[\frac{1}{Q} e_{pq}\left(\overset{t}{\underset{\tau=0}{t,\tau}}\right)\right]}_{Q \text{ times}} = QF_{ij}\left[\frac{1}{Q} e_{pq}\left(\overset{t}{\underset{\tau=0}{t,\tau}}\right)\right]$$

Hence Boltzmann superposition guarantees the following two conditions

$$F_{ij}\left[Pe_{pq}\left(\overset{t}{\underset{\tau=0}{t,\tau}}\right)\right] = PF_{ij}\left[e_{pq}\left(\overset{t}{\underset{\tau=0}{t,\tau}}\right)\right], \text{ and} \tag{2.16a}$$

$$F_{ij}\left[\frac{1}{Q} e_{pq}\left(\overset{t}{\underset{\tau=0}{t,\tau}}\right)\right] = \frac{1}{Q} F_{ij}\left[e_{pq}\left(\overset{t}{\underset{\tau=0}{t,\tau}}\right)\right]. \tag{2.16b}$$

Using the principle of superposition repeatedly it can now be shown that

$$F_{ij}\left[re_{pq}\left(\overset{t}{\underset{\tau=0}{t,\tau}}\right)\right] = rF_{ij}\left[e_{pq}\left(\overset{t}{\underset{\tau=0}{t,\tau}}\right)\right], \tag{2.17}$$

where r = rational number.

Thus it is seen there is only one mathematical requirement for linearity if a reasonable form of continuity requirement is enforced, and that is Boltzmann superposition. It can be shown also that scalar multiplication in no way implies superposition.

In fact scalar multiplication is simply a homogeneity condition of degree one in the constitutive law, and many non-linear differential equations, functions, and functionals are homogeneous but not linear. By homogeneity of degree n it is meant that a mathematical operation, say $f(x,y,z)$, has the property [35]

$$f(ax,ay,az) = a^n f(x,y,z). \tag{2.18}$$

If a function has this property, differentiation with respect to the scalar a, and evaluation at a equal unity produces Euler's equation [35]

$$nf = x\frac{\partial f}{\partial x} + y\frac{\partial f}{\partial y} + z\frac{\partial f}{\partial z}. \tag{2.19}$$

An example of a function that is non-linear but homogeneous to degree one, hereafter referred to simply as homogeneous, is

$$f(x,y,z) = x^3 \big/ (x^2 + y^2 + z^2). \tag{2.20}$$

Non-linear ordinary differential equations having this property can always be separated [35] and solved quite simply by choosing a new variable that is the ratio of the two variables in the equation. Examples of functional equations that are homogeneous but not linear also can be constructed [28,34]. The main difficulty

that arises from this observation is the commonly used and stated criteria for linearity of elastic and viscoelastic materials is, "doubling the strain input doubles the stress output" [19]. In light of the linearity conditions it is seen that this is only a check on the homogeneity of the materials constitutive law which is a necessary condition for linearity, but in itself cannot guarantee linearity. The homogeneity condition demands that the relaxation modulus for a linear viscoelastic material be independent of the magnitude of the applied strain, or that the first stretch behavior of an elastic solid have a constant moduli. These are necessary conditions for linearity but not sufficient conditions. Materials that possess this homogeneity property but are still non-linear perhaps are the simplest non-linear materials since at least one of the conditions of linearity is satisfied. Because one of the linearity conditions has been satisfied, the material will possess some of the properties of linear materials. Unfortunately, the standard characterization methods used by many laboratories will cause all homogeneous materials, linear or non-linear, to be characterized as linear materials [1,2]. Examples of a non-linear viscoelastic material having a homogeneous constitutive law are solid propellants and most highly filled polymeric materials [1,2] such as asphalt concrete. Examples of non-linear elastic* materials having homogeneous constitutive laws are steel wire [36], rock [37], portland cement and masonry materials.

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*Elastic is used in the classical sense which means complete recovery of geometry when the tractions are removed.

For non-linear elastic materials possessing homogeneous constitutive laws, linear elastic analysis can be shown to be applicable so long as the material has never been deformed, superposition is not required, and the stresses during unloading are not required. In other words, it is equivalent to using non-linear elastic theory for the first stretch plasticity. Both cases should yield valid results for the first loading but will give erroneous results for unloading.

For non-linear viscoelastic materials possessing homogeneous constitutive laws little can be said about the behavior as will become evident later. If all the time effects are of the Boltzmann-Volterra heredity integral type [29,30], then and only then will linear viscoelasticity yield the proper results for the first stretch behavior. If the time effects are not of the type mentioned above, then linear viscoelastic analysis will only give the proper solution for a single step input.

The purpose of this thesis is to develop constitutive equations for non-linear materials having homogeneous constitutive equations of degree one with and without time effects and to demonstrate how simply they can be used in solving boundary valued problems. Before proceeding, however, some discussion of the so-called Fréchet multiple integral expansion is in order since it supposedly represents a general expansion of a simple material [29,30].

III. INADEQUACIES OF CURRENT NON-LINEAR THEORIES

3.1 The Fréchet Expansion

During the last decade considerable advances have been made in formulating constitutive equations to represent the mechanical behavior of non-linear viscoelastic materials [21-33,38-40]. The foundation for the theoretical investigations of non-linear materials with memory was first formulated by Volterra [28], Green and Rivlin [29], Noll [38], and Pipkin [39]. This work was concerned with a class of materials known as simple materials [26,27]. A simple material is defined as a material in which the state of stress at time t, $S_{ij}(t)$, can be expressed as some functional of the deformation gradient. Using arguments similar to those employed by Fréchet [28,41] in 1910, Green, Rivlin and Pipkin have demonstrated that a continuous tensor valued functional, (a functional of several variables some of which are components of a tensor) may be approximated by a functional power series of homogeneous tensor valued functionals. Fréchet's contribution is a generalization of the Weirstrass theorem [42] stating a continuous function may be approximated by a polynomial. Volterra [28] made use of Fréchet's work for non-linear functionals of one variable and for linear functionals of several variables. In his book, Volterra [28] suggests that all hereditary phenomenon in the mechanics of materials could be taken into account if the constitutive equation was expressed as

$$S_{ij}(t) = F_{ij}\left[\underset{\tau=0}{\overset{t}{e_{11}(t,\tau)}}, \underset{\tau=0}{\overset{t}{e_{22}(t,\tau)}}, \underset{\tau=0}{\overset{t}{e_{33}(t,\tau)}}, \underset{\tau=0}{\overset{t}{e_{12}(t,\tau)}}, \underset{\tau=0}{\overset{t}{e_{13}(t,\tau)}}, \underset{\tau=0}{\overset{t}{e_{23}(t,\tau)}}\right] =$$

$$F_{ij}\left[\underset{\tau=0}{\overset{t}{e_{pq}(t,\tau)}}\right] \tag{3.1}$$

He indicated that this functional relationship could be expanded in the Fréchet type of multiple integral expansion. Giving only the linear terms in the expansion Volterra indicated a general regular linear* hereditary material could be expressed as

$$S_{ij}(t) = A_{ijk\ell}(t)e_{k\ell}(t) + \int_0^t D_{ijk\ell}(t,\tau)e_{k\ell}(\tau)d\tau \tag{3.2}$$

Equation (3.2) is an integral constitutive equation for an aging linear anisotropic viscoelastic solid.

Green, Rivlin and Pipkin have since extended Volterra's work by including the non-linear terms in the expansion. The resulting equation in the case of small deformation was given as

$$\begin{aligned} S_{ij}(t) = &\int_0^t K_{ijp_1q_1}(t,\tau_1)\dot{e}_{p_1q_1}(\tau_1)d\tau_1 + \\ &\int_0^t\int_0^t K_{ijp_1q_1p_2q_2}(t,\tau_1,\tau_2)\dot{e}_{p_1q_1}(\tau_1)\dot{e}_{p_2q_2}(\tau_2)d\tau_1 d\tau_2, + \cdots \\ &+\int_0^t\cdots\int_0^t K_{ijp_1q_1\cdots p_nq_n}(t,\tau_1,\cdots\tau_n)\dot{e}_{p_1q_1}(\tau_1)\cdots\dot{e}_{p_nq_n}(\tau_n)d\tau_1\cdots d\tau_n + \cdots \end{aligned} \tag{3.3}$$

*Equation (3.2) is not the most general linear relationship, (e.g., it does not contain the general linear differential operator equation of linear viscoelasticity [19]). It is however the most general integral relationship. These additional non-integral linear terms were called "irregular" by Volterra [28].

The manner in which this equation is developed is quite simple [29,43]. Consider that the stress $S_{ij}(t)$ is only a function of the strain at N discrete points in time τ_m, where $\tau_m < \tau_{m+1}$, $1 \leq m \leq N$, $\tau_N = t$. This function would therefore be an approximation to the behavior of a simple material. Representing this function by a general polynomial yields

$$S_{ij}(t) = \sum_{r_1=1}^{N} C_{ijp_1q_1}(t,\tau_{r_1})e_{p_1q_1}(\tau_{r_1}) +$$

$$+ \sum_{r_1=1}^{N} \sum_{r_2=2}^{N} C_{ijp_1q_1p_2q_2}(t,\tau_{r_1},\tau_{r_2})e_{p_1q_1}(\tau_{r_1})e_{p_2q_2}(\tau_{r_2}) +$$

$$+ \sum_{r_1=1}^{N} \cdot\cdot \sum_{r_n=1}^{N} C_{ijp_1q_1\cdot\cdot p_nq_n}(t,\tau_{r_1},\cdot\cdot\tau_{r_n})e_{p_1q_1}(\tau_{r_1})\cdot\cdot e_{p_nq_n}(\tau_{r_n}) +\cdot\cdot \tag{3.4}$$

By letting the number of discrete times N increase to infinity, the equation goes to the limit of complete history dependence. Thus, the above summations become functionals over the interval $0 \leq \tau \leq t$. In addition special dependency must be allowed for the values of strain taken at time t, $e_{pq}(t)$ which is called the "exceptional point" (see Volterra [28] page 15). By allowing N to increase to infinity, equation (3.4) becomes

$$S_{ij}(t) = A_{ijp_1q_1}(t)e_{p_1q_1}(t) + A_{ijp_1q_1p_2q_2}(t)e_{p_1q_1}(t)e_{p_2q_2}(t) + \cdots$$

$$+ \int_0^t C_{ijp_1q_1}(t,\tau_1)e_{p_1q_1}(\tau_1)d\tau_1 +$$

$$+ \int_0^t \int_0^t C_{ijp_1q_1p_2q_2}(t,\tau_1,\tau_2)e_{p_1q_1}(\tau_2)e_{p_2q_2}(\tau_2)d\tau_1 d\tau_2 + \cdots \tag{3.5}$$

Equation (3.5) is equivalent to equation (3.3), and one equation can be obtained from the other by integrating by parts [44]. Both forms will be used in this thesis, but equation (3.3) will be preferred since it is the most compact notation.

Equation (3.3) according to Green, Rivlin and Pipkin, represents a general simple material [38,39], providing the strain histories and the functionals are continuous. The equation surely describes an anisotropic non-linear time-dependent material with aging; however, whether the expansion is useful to describe all non-linear simple materials has not been shown. They indicate that the functional represented by the above expansion may be approximated with any degree of accuracy simply by adding more terms in the expansion [29], just as the Weirstrass theorem indicates a continuous function may be approximated uniformly to any desired degree of accuracy by simply adding more terms in the polynomial. From such statements the impression is given that by taking a large number of terms in the expansion one might approximate all types of behavior quite well. However, such is not the case. Equation (3.3) was obtained by purely mathematical methods to approximate the continuous functional given in equation (3.1), linear

or non-linear. One simple demonstration that this particular representation cannot approximate some types of non-linear behavior is given below.

Mathematically, there are two requirements for linearity [28]. These requirements are homogeneity and additivity. If a constitutive functional is linear it must satisfy these two conditions for all times t, all strain inputs $e_{pq}(\tau)$, and all real scalars a. A functional that obeys the homogeneity principle and not the additivity principle is not linear, although it does have some properties similar to linear functionals. Such a functional is known as a homogeneous functional of degree one [28,23]. A homogeneous functional of degree n would be given by [28,23]

$$F_{ij}\left[ae_{pq}\overset{t}{\underset{\tau=0}{(t.\tau)}}\right] = a^n F_{ij}\left[e_{pq}\overset{t}{\underset{\tau=0}{(t,\tau)}}\right] ,$$

where n = positive integer. (3.6)

Since Volterra, Green, Rivlin, and others indicate (3.3) is a general expansion for a continuous functional, the expansion should contain this type of non-linearity. Solid propellant materials [1,2] and other granular media appear to have homogeneous constitutive equations of degree one but not linear equations. They can have relaxation moduli that do not depend upon strain magnitude, yet these materials do not obey the additivity requirement. Consider for simplicity the non-linear homogeneous functional of a single variable $x(t,\tau)$ given by

$$y(t) = G\left[\underset{\tau=0}{\overset{t}{x(t,\tau)}}\right] , \tag{3.7}$$

which by definition obeys the homogeneity principle

$$G\left[\underset{\tau=0}{\overset{t}{ax(t,\tau)}}\right] = aG\left[\underset{\tau=0}{\overset{t}{x(t,\tau)}}\right] , \tag{3.8a}$$

and does not obey the additivity principle

$$G\left[\underset{\tau=0}{\overset{t}{x_1(t,\tau)}} + \underset{\tau=0}{\overset{t}{x_2(t,\tau)}}\right] \neq G\left[\underset{\tau=0}{\overset{t}{x_1(t,\tau)}}\right] + G\left[\underset{\tau=0}{\overset{t}{x_2(t,\tau)}}\right]. \tag{3.8b}$$

Expanding the right hand side of equation (3.8a) in a Fréchet expansion

$$\begin{aligned} aG\left[\underset{\tau=0}{\overset{t}{x(t,\tau)}}\right] &= aK_0(t) + a\int_0^t K_1(t,\tau_1)\dot{x}(\tau_1)d\tau_1 + \\ &+ a\int_0^t\int_0^t K_2(t,\tau_1,\tau_2)\dot{x}(\tau_1)\dot{x}(\tau_2)d\tau_1 d\tau_2 + \\ &+ a\int_0^t \cdots \int_0^t K_n(t,\tau_1,\cdots\tau_n)\dot{x}(\tau_1)\cdots\dot{x}(\tau_n)d\tau_1\cdots d\tau_n + \cdots \end{aligned} \tag{3.9}$$

Expanding the left hand side of equation (3.8a) in a Fréchet expansion yields

$$\begin{aligned} G\left[\underset{\tau=0}{\overset{t}{ax(t,\tau)}}\right] &= K_0(t) + a\int_0^t K_1(t,\tau_1)\dot{x}(\tau_1)d\tau_1 + a \\ &+ a^2\int_0^t\int_0^t K_2(t,\tau_1,\tau_2)\dot{x}(\tau_1)\dot{x}(\tau_2)d\tau_1 d\tau_2 + \\ &+ a^n\int_0^t K_n(t,\tau_1,\cdots,\tau_n)\dot{x}(\tau_1)\cdots\dot{x}(\tau_n)d\tau_1\cdots d\tau_n + \cdots \end{aligned} \tag{3.10}$$

The second terms in equations (3.9) and (3.10) are identical, but they are linear and obey both scalar multiplication and additivity. To have a homogeneous functional of degree one, yet a non-linear functional, the difference between these two equations must be identically zero for all scalars a, for all arbitrary $x(\tau)$, and for all time t. For this condition to be satisfied requires that

$$0 = (a-1)K_0(t) + (a^2-a)\int_0^t\int_0^t K_2(t,\tau_1,\tau_2)\dot{x}(\tau_1)\dot{x}(\tau_2)d\tau_1 d\tau_2 +$$

$$\cdot\cdot + (a^n-a)\int_0^t\cdot\cdot\int_0^t K_n(t,\tau_1,\tau_2,\cdot\cdot\tau_n)\dot{x}(\tau_1)\cdot\cdot(\tau_n)d\tau_1\cdot\cdot d\tau_n + \cdot\cdot \tag{3.11}$$

If a material has this property the kernel functions may be assumed known since they are material properties. Choosing a history $x_1(\tau)$ and evaluating each term at some time t_1, a polynomial of degree n is obtained assuming the original expansion is truncated at the n^{th} term. This truncation will give at most n values of the scalar a for which equation (3.8a) is satisfied. Increasing the time to t_2 or change the history to $x_2(\tau)$ results in another set of roots, presumably different from the first. Therefore if the series is truncated, scalar multiplication can hold only for a certain number of scalars and these will change with time. Also, it should be pointed out that for any set of kernel functions whenever the series is terminated a set of scalars for which scalar multiplication will hold at some particular time can always be obtained.

There are only two ways in which it is possible for scalar multiplication to hold for all scalars using the Fréchet expansion. One way is for the material to be linear and then every kernel function in equation (3.11) is zero and superposition holds. The second way is to admit an infinite number of terms in the expansion. In the second case if the infinity of roots obtained fills the set of real numbers the condition will be satisfied. This latter case is not worth considering since the value of a series expansion is questioned if every term must be used. The Fréchet expansion is therefore not a good approximation for the class of materials having non-linear homogeneous constitutive equations of degree one.

It may be argued that perhaps such materials do not exist. This argument is not valid for three reasons: (1) simple equations can be constructed which have the indicated properties and satisfy all the requirements stated in obtaining such an expansion; (2) the expansion was obtained on purely mathematical grounds, and should contain this type of non-linearity; (3) there are materials which appear to have the indicated properties. One interesting point about any that could be constructed for such materials is that they are all permanent memory constitutive equations and interestingly enough, the materials possessing this property also are permanent memory materials. A permanent memory material is defined in this thesis as a material in which the current state of stress or strain will always be dependent on past states.

For non-aging materials, Volterra [28] and Green and Rivlin [29] demonstrated that the kernel functions should be of the form

$$K_n(t,\tau_1,\tau_2,\cdot\cdot\tau_n) = K_n(t-\tau_1,t-\tau_2,\cdot\cdot,t-\tau_n) \ . \tag{3.12}$$

The output for two strain inputs differing only by a time shift also will differ by the same time shift when the kernels are written in this manner. With reference to non-aging materials, Green and Rivlin have assumed fading memory [29,46] kernel functions in their alternate derivations of this theory. In these alternate derivations the stress at time t is expressed in terms of the time derivatives of strain evaluated at the current time. This non-linear form involving various combinations of the derivatives is to the Fréchet expansion what the linear differential operator equation is to the Boltzmann Integral [45,47]. To obtain these equations, Green and Rivlin assumed that the kernel functions were zero if any of their arguments, $t-\tau_i$, became greater than some fixed time T [29]. Physically the time T is a measure of the limits of memory. This idea describes one concept of fading memory and is a property many materials do not exhibit. If the kernel functions have this property of a limited memory and one considers the output to some input $e_{pq}(\tau)$ with the property that

$$e_{pq}(\tau) = e_{pq}(\tau+h) \ , \tag{3.13}$$

where $h > T$, then it can be shown that using the Fréchet expansion [28,29] the stress output has the property

$$S_{ij}(t) = S_{ij}(t+h) \ . \tag{3.14}$$

Physically fading memory means that there are no irreversible physical effects caused by the history of deformation since any effect can be negated by simply allowing the material to rest in the undisturbed state for a time greater than T [25,28,29,33]. Many rheologists are under the impression that during stress relaxation testing if the stress relaxes to come constant value, then fading memory is implied, but this is not the case. It, like so many things, is a necessary requirement, but not a sufficient one.

3.2 Isotropic Theories of Non-Linear Viscoelasticity

The theory of Green, Rivlin and Pipkin discussed in the previous sections was for anisotropic solids. If the material is a non-aging material and originally isotropic in the undeformed state, Rivlin [36] and Pipkin [29] have shown that the equation may be expressed as

$$
\begin{aligned}
\underline{S}(t) = & \int_0^t \{\underline{I}k_1 \mathrm{tr}\dot{\underline{e}}(\tau_1) + k_2\dot{\underline{e}}(\tau_1)\}d\tau_1 + \int_0^t\int_0^t \underline{I}k_3 \mathrm{tr}\dot{\underline{e}}(\tau_1)\mathrm{tr}\dot{\underline{e}}(\tau_2) \\
& + \underline{I}k_4 \mathrm{tr}[\dot{\underline{e}}(\tau_1)\dot{\underline{e}}(\tau_2)] + k_5\dot{\underline{e}}(\tau_1)\mathrm{tr}\dot{\underline{e}}(\tau_2) + k_6\dot{\underline{e}}(\tau_1)\dot{\underline{e}}(\tau_2)\}d\tau_1 d\tau_2 \\
& + \int_0^t\int_0^t\int_0^t \{\underline{I}k_7 \mathrm{tr}\dot{\underline{e}}(\tau_1)\mathrm{tr}\dot{\underline{e}}(\tau_2)\mathrm{tr}\dot{\underline{e}}(\tau_3) + \underline{I}k_8 \mathrm{tr}\dot{\underline{e}}(\tau_1)\mathrm{tr}[\dot{\underline{e}}(\tau_2)\dot{\underline{e}}(\tau_3)] \\
& + k_9\dot{\underline{e}}(\tau_1)\mathrm{tr}\dot{\underline{e}}(\tau_2)\mathrm{tr}\dot{\underline{e}}(\tau_3) + k_{10}\dot{\underline{e}}(\tau_1)\,\mathrm{tr}[\dot{\underline{e}}(\tau_2)\dot{\underline{e}}(\tau_3)] \\
& + k_{11}\dot{\underline{e}}(\tau_1)\dot{\underline{e}}(\tau_2)\mathrm{tr}\dot{\underline{e}}(\tau_3) + k_{12}\dot{\underline{e}}(\tau_1)\dot{\underline{e}}(\tau_2)\dot{\underline{e}}(\tau_3)\}d\tau_1 d\tau_2 d\tau_3 + \int_0^t\int_0^t\int_0^t\int_0^t \cdots
\end{aligned}
\qquad (3.15)
$$

In the above equation k_1, k_2 are functions of $(t-\tau_1)$; k_3, k_4, k_5, k_6 are functions of $(t-\tau_1, t-\tau_2)$; and $k_7, \cdots, k_{12}$ are functions of $(t-\tau_1, t-\tau_2, t-\tau_3)$; etc. To obtain this equation they showed that the equation for an isotropic material could be written as

$$\underline{S}(t) = K_0\underline{I} + \int_0^t K_1(t-\tau_1)\dot{\underline{e}}(\tau_1)d\tau_1 + \int_0^t\int_0^t K_2(t-\tau_1, t-\tau_2)\dot{\underline{e}}(\tau_1)\dot{e}(\tau_2)d\tau_1 d\tau_2$$

$$+\cdots + \int_0^t \cdots \int_0^t K_n(t-\tau_1, t-\tau_2, \cdots, t-\tau_n)\dot{\underline{e}}(\tau_1)\cdots\dot{\underline{e}}(\tau_n)d\tau_1\cdots d\tau_n + \cdots , \tag{3.16}$$

where the kernel function $K_0, K_1, \cdots K_n$ are functions of the history of the three strain invariants $\overset{t}{\underset{0}{I_1(\xi)}}, \overset{t}{\underset{0}{I_2(\xi)}}$, and $\overset{t}{\underset{0}{I_3(\xi)}}$ as well as the variables $t-\tau_i$. Instead of using the history of the invariants which involves combinations of the strains, they expressed these histories in terms of the traces of the tensors which is an equivalent form since $\mathrm{tr}\underline{e}$, $\mathrm{tr}\underline{e}^2$, and $\mathrm{tr}\underline{e}^3$ form an integrity basis for the three scalar invariants [29,30,44]. Then they expanded each kernel in a Fréchet expansion and equation (3.15) is what remains after all the terms are gathered. It should be pointed out again that in the limit of small strains, equation (3.15) reduces to linear viscoelasticity. Also it is seen that when the kernel functions in equation (3.16) are only functions of the current value of the invariants and not their histories, and are also constant functions of the variables $t-\tau_i$, the integrations can be performed giving

$$\underline{S} = k_0\underline{I} + k_1\underline{e}^2 + k_2\underline{e}^2 + k_3\underline{e}^3 + \cdots + k_n\underline{e}^n + \cdots \qquad (3.17)$$

where the k_i are functions of the three scalar strain invariants evaluated at the current time t. Applying the Cayley-Hamilton Theorem [25,27], which states a tensor must satisfy its own characteristic equation, gives the equality

$$\underline{e}^3 = I_1\underline{e}^2 + I_2\underline{e} + I_3\underline{I} \ . \qquad (3.18)$$

Hence one sees that any power of the strain tensor higher than degree two can be expressed in terms of the $\underline{e}^2$, $\underline{e}$, $\underline{I}$ and the scalar invariants I_1, I_2, and I_3. Equation (3.17) can be reduced to

$$\underline{S} = \psi_0\underline{I} + \psi_1\underline{e} + \psi_2\underline{e}^2 \quad , \qquad (3.19)$$

where ψ_0, ψ_1, ψ_2 are arbitrary functions of the invariants of $\underline{e}$.

Equation (3.19) is the constitutive equation describing the most general non-linear isotropic elastic solid [26,32]. Written in component form this becomes

$$S_{ij} = \psi_0\delta_{ij} + \psi_1 e_{ij} + \psi_2 e_{ik}e_{kj} \qquad (3.20)$$

From this equation it can be readily seen that the principle stresses and the principle strains have the same directions because when all the shear strains become zero, so do the shear stresses.

Equation (3.20) is elastic in that the stresses are only a function of the current strain tensor and independent of any previous values of the tensor. Elasticity is a theory with no memory of past deformation states and is naturally contained in the fading memory viscoelasticity. In equation (3.16) it was stated that the kernels were functionals of the history of the invariants and that these functionals were expanded by the Fréchet expansion to obtain equation (3.15). As pointed out earlier the Fréchet expansion cannot simply describe some types of non-linearities. One of the reasons the expansion is used is that it is objective [25,26,27]. Objectivity in continuum mechanics means that the forces acting on an element resulting from some strain history must be invariant to arbitrary rotations and translations of the coordinate systems. Green and Rivlin have shown that the Fréchet expansion has this property so long as the strains are given by an objective measure of strain such as the Green or Cauchy strain tensors [29]. Since the invariants are by definition invariant with respect to rotations and the strains are gradients of motion a translation also has no effect on their magnitudes, so it is permissible to have the kernels be any functional of the history of the invariants. In particular homogeneous but non-linear integral representations of viscoelasticity can be constructed within the framework of the Green-Rivlin theory so long as specific functional forms are chosen.

3.3 Other Non-Linear Constitutive Equations

There are many types of non-linear constitutive equations. For viscoelastic phenomenon these equations are usually of the integral type. Some of these equations are similar but are developed from different approaches.

Herrmann recently developed an energy approach to non-linear viscoelasticity [43]. He assumed the material was capable of instantaneous deformations and not capable of instantaneous energy dissipation. He has shown that with these two restrictions, the stress at time t, $S_{ij}(t)$ is the derivative with respect to the strain $e_{ij}(t)$ of an energy functional. The resulting constitutive equations for both isotropic and anisotropic material behavior are the same as those developed by Green, Rivlin and Pipkin. The energy approach taken by Herrmann therefore appears to restrict the valid application of the constitutive equation discussed in sections 3.1 and 3.2 to materials capable of instantaneous deformations but not capable of instantaneous energy dissipation.

Schapery has derived a single integral representation [48,49] that has proven very useful in describing some types of permanent memory behavior. His work was founded on an irreversible thermodynamic development and his equation has a form similar to the Boltzmann superposition integral representation of linear viscoelasticity. Roughly speaking, Schapery's non-linear theory incorporates all the non-linearities in a distorted time scale. Rather than using the current time t and the dummy time τ in his integral representation he

uses a reduced current time ξ and a reduced dummy time ξ'. These reduced times are given as functionals of the temperature-time and strain-time histories. These equations appear to be especially applicable for characterizing plastic type materials. Schapery has shown that rate independent plasticity and some types of viscoplasticity are within the range of applicability of his equations. He has also applied them to materials such as solid propellants [16,48,49]. Analysis of his equations however indicate it would be difficult to contain the homogeneous non-linear constitutive equation discussed in this thesis within the framework of his theory.

Coleman and Noll [21], Lianis [50] and others [51,52,53] have contributed considerably to the theory of non-linear viscoelasticity as applied to solids and liquids alike. All of their theories are based on the principle of fading memory which is valid for amorphorus polymers or liquids but excludes a great many materials. Unlike the work of Green and Rivlin and Pipkin, the work of Coleman, Noll, and Lianis has been mostly concerned with non-isothermal conditions and the additional restrictions placed on the constitutive theory from the laws of thermodynamics. The representations used by these researchers are in general a simplification of those proposed by Green and Rivlin. Since this paper is not concerned with fading memory viscoelasticity, their work on the thermoviscoelastic behavior of fading memory materials contributes little to describing permanent memory phenomenon.

IV. MODELING THE MULLINS' EFFECT IN FILLED POLYMERS

Viscoelastic materials have a "memory": that is, their present state depends upon their entire past history. Nearly all of the integral viscoelastic constitutive theories used to date for polymeric materials such as solid propellants are based on the concept of "fading memory". This means that a material is more sensitive to its immediate past than to their distant past. A physical interpretation of fading memory constitutive laws, both linear and nonlinear, indicates that such materials tend to forget the distant past. This theory implies no permanent change in microstructure, or damage caused by the deformation. A fading memory material can undergo no irreversible changes in structure and can be thought of as attributing the time effects, such as relaxation and creep, to internal viscosity.

Experience indicates that propellants do not fall into the category of fading memory materials even at small strains below detectable dewetting [1,2] or volume dilatation. Propellants suffer from the "Mullins' Effect" [2-8], which is a stress-softening that occurs with deformation, and causes a permanent hysteresis on repeat loading.

There is considerable evidence that all the hysteresis effects observed in propellants and most of the viscoelastic behavior are caused by the time dependent failure of the polymer on a molecular basis and are not due to internal viscosity [1,2]. At near equilibrium rates and small strains, propellants exhibit the same type of hysteresis that many lowly filled, highly cross-linked rubbers demonstrate at

large strains [1-8]. This phenomenon is called the "Mullins' Effect" and has been attributed to microstructural failure. Mullins postulated that a breakdown of particle-particle association and possibly also particle-polymer breakdown could account for the effect [3-5]. Later Bueche [7,8] proposed a molecular model for the "Mullins' Effect" based on the assumption that the centers of the filler particles are displaced in an affine manner during deformation of the composite. Such deformations would cause a highly non-uniform strain and stress gradient in the polymer between particles, especially in the direction of stretch. He assumed that polymer chains attached themselves at both ends to neighboring filler particles and that these chains ruptured when the particles were separated enough to extend the chains to near their full elongation. He derived a model from which he could calculate the difference in stress levels at a given elongation for the first and second stretching cycles [7]. It is this type of model that is generally accepted as being representative of the molecular behavior which causes the "Mullins' Effect". Figure 4.1 illustrates this behavior for repetitive stretching to increasing strain levels. In highly cross-linked rubbers, the effect only depends upon strain and is generally irreversible [5,6,59]. However, if the prestressed composite is allowed to rest for long times in the relaxed state, a portion of the original stiffness might be regained [5,59]. This recovery or rehealing appears to be a complex function of the recovery temperature and time, nevertheless, it can and does greatly influence the materials behavior.

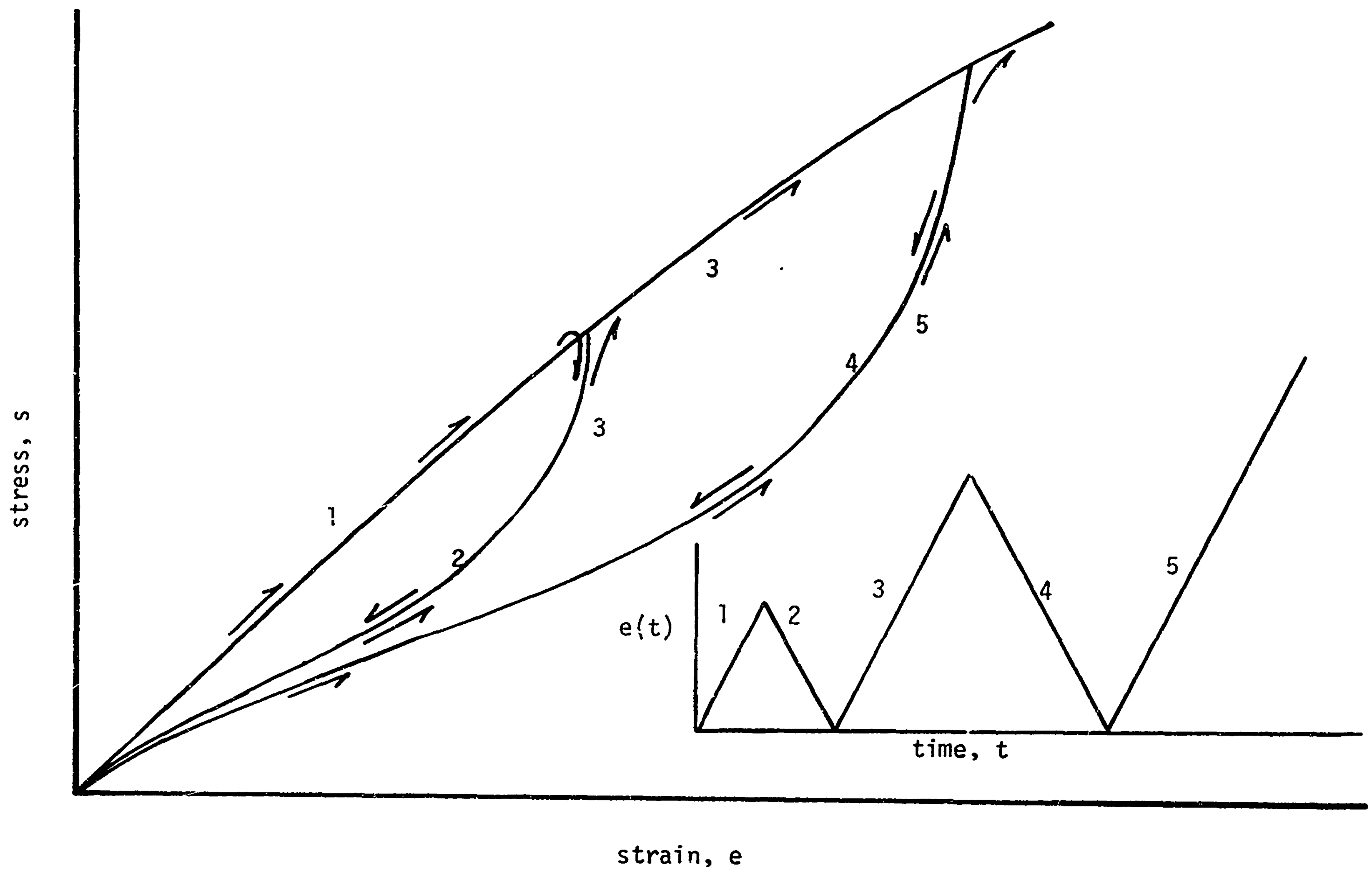


Figure 4.1. TYPICAL PROPELLANT EQUILIBRIUM STRESS-STRAIN BEHAVIOR WHEN THE DIRECTION OF STRAIN IS REVERSED.

All of the theoretical and nearly all of the experimental work done in studying this phenomenon has been on materials similar to the rubber found in automobile tires. These are highly cross-linked rubbers that are usually filled to about 20 volume percent with very fine carbon black. Propellants, on the other hand, are lowly cross-linked and highly filled with coarse particles. The relative particle spacing is consequently much more severe and the polymer chains are on the average hundreds of times longer in propellants than in tire rubber. The probability of finding a larger portion of the chains connecting particles would be greater in propellants and the effect therefore should be much stronger and occur at smaller strains [1,2,6], but the same basic mechanism proposed by Bueche still applies. This polymeric chain failure is therefore the step which precedes the vacuole formation process which causes the stress and dilatational non-linearities observed at larger strains [9,10]. Multiple stretch data on propellants at large strains with and without a superimposed pressure environment demonstrate that propellants also exhibit the Mullins' type hysteresis at large strains in the absence of measurable dilatation [6].

The time independent "Mullins' Effect" can account for the near equilibrium hysteresis observed in propellants at low strains, but cannot account for the nonlinear time effects [1,2]. There is considerable evidence however, that the "Mullins' Effect" in propellants is a very strong function of time [1,2]. Time dependent chain failure can be readily demonstrated by simply examining some of the routine tests run on solid propellants and also examining the influence of filler on the viscosity of a given polymer.

One of the simplest ways of demonstrating a time dependent "Mullins' Effect" is through the strain endurance test [1,19]. In this test, a sample is strained to some level and held there for several days or longer. The only measurement taken is the time to failure, if the sample fails within the test period. The point of interest here is that samples fail while held at conditions of constant strain when the stress is slowly relaxing or at most constant. This type of failure is clear evidence of a time dependent "Mullins' Effect" and also demonstrates that some portion of the time dependent stress relaxation must be due to chain failure.

Another example of a time dependent "Mullins' Effect" is that of a lowly cross-linked polymer, with little or no time dependency when unfilled, which becomes significantly time dependent when filled [53], as shown in figure 4.2. The more filler incorporated into the system, the more marked the time effect. Many propellant polymers fall into this category and nearly all propellants show time dependence over such long times that true equilibrium data cannot be obtained. This time dependence in the composite material and no time dependence in the unfilled polymer cannot be explained by the argument that the polymeric strain rates are higher in the composite than in the pure polymer since the time effects continue for such long times, and many propellant binders show no time dependence even at very short times.

Tests such as those described above indicate that the constitutive equations and degree of microstructural damage must be highly coupled effects. One of the existing concepts now being used to predict

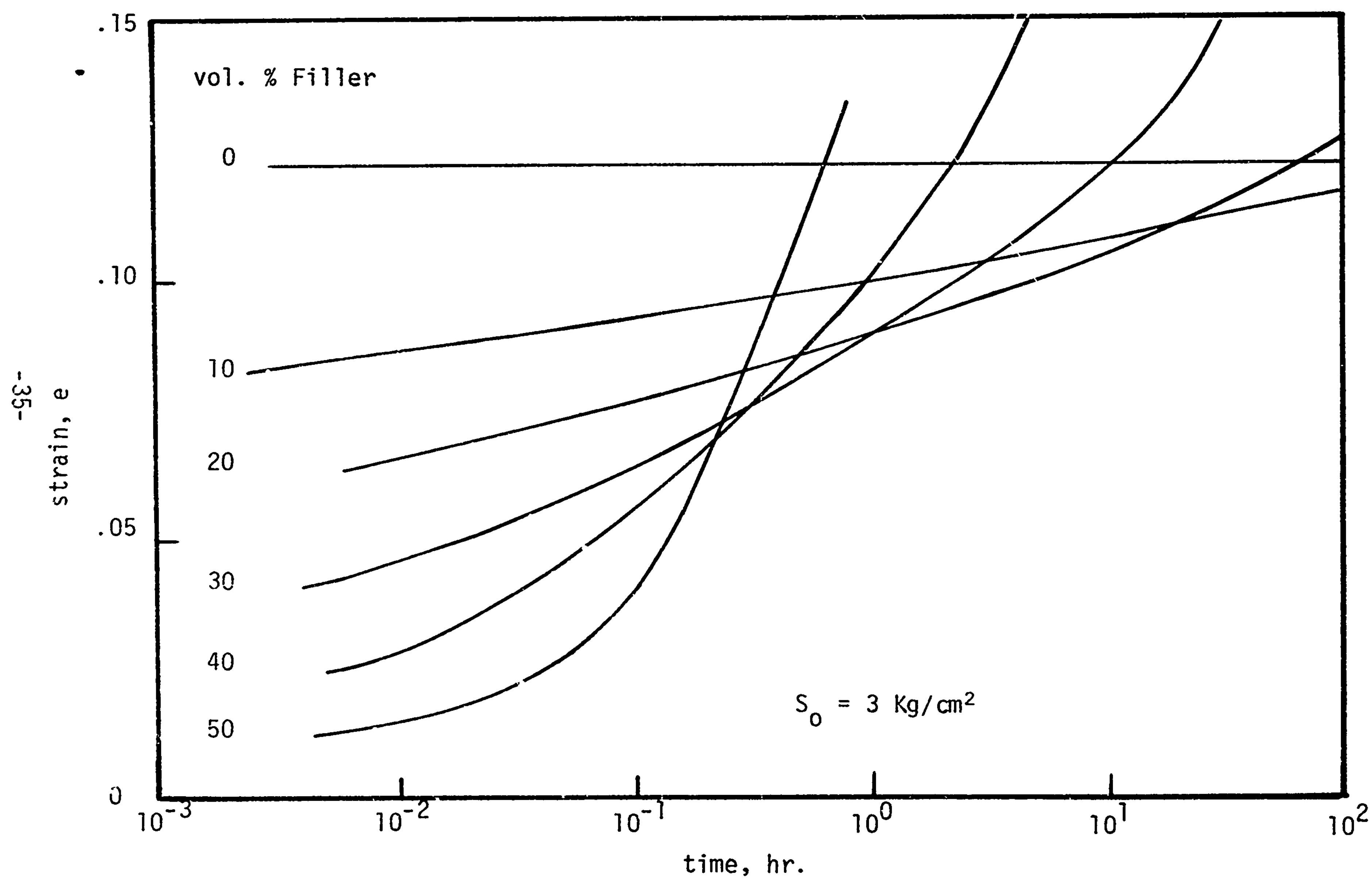


Figure 4.2. CREEP OF SODIUM CHLORIDE FILLED POLYURETHANE RUBBER.

failure in propellants calculates the state of stress using fading memory constitutive theory and then uses these calculated stresses in cumulative damage relations to predict failure [54,55]. The assumption that the degree of damage and the constitutive equation are uncoupled can only lead to erroneous results for materials exhibiting the "Mullins' Effect". The model discussed below describes the "Mullins' Effect" and clearly demonstrates the coupling between the constitutive equation and the degree of damage. The model provides insight into the mechanism of behavior and indicates key variables or measures that should be used in the general multidimensional constitutive equation.

4.1 Modeling the Time Independent "Mullins Effect"

There have been various models and mechanisms proposed for the "Mullins' Effect". Bueche proposed a model based on chains failing due to physically non-homogeneous local deformations [7,8]. His model was not sufficiently general and was designed to prove whether the chains were unbonding from the filler or actually failing. In this section a general one dimensional model will be developed for the "Mullins' Effect". Before proceeding, it would be wise to clarify the main difference between filled and unfilled polymers. The equilibrium constitutive equation for cross-linked amorphous polymers has been developed from the statistical theory of rubber elasticity assuming ideal rubber behavior [56,57]. There are six basic assumptions made in the development of the statistical theory of ideal rubber behavior. They are:

1. There is no change in internal energy with isothermal deformations.
2. The end-end displacement of a polymer chain is small compared to its actual length.
3. The relative end-end displacements $(\lambda_x, \lambda_y, \lambda_z)$ of all polymer chains in the system are equal for homogeneous motions.
4. The relative chain deformations occuring microscopically are the same as the deformation of the body for homogeneous motions.
5. There is no interaction between polymer chains.
6. A polymer chain never fails.

These assumptions dictate that the configurational entropy associated with a polymer chain be given by a Gaussian distribution and enable simple addition of the contributions of each chain. The Gaussian distribution is only valid for end-end chain displacements that are small compared to the actual chain length since they actually allow for end-end displacements from zero to infinity [56,57]. Corrected configurational statistics for large deformations provide what is called the Langevin Function [57]. The Langevin Function provides the correct configurational entropy since it limits the end-end separation of a chain to the chains actual length [57]. The Gaussian distribution appears as the first term in the Langevin Function which is essentially a virial expansion. The main difference between these two distributions is the force-deformation relation they give for

a polymer chain [57] which is illustrated in figure 4.3. The great stiffening experienced when a chain is near fully extended can be simply observed by stretching a rubber band to failure.

The main difference between filled and unfilled systems is that even under equilibrium conditions the relative end-end displacement of all polymer chains in the system are not equal. Instead one finds, by any form of analysis, that the local strains in a filled system subjected to a physically homogeneous deformation are a very strong function of filler content, position, particle shape, and the distribution of chain lengths. The prime reason for the physically non-homogeneous local deformations of the polymer is that it is the centers of the filler particles that must undergo near affine or similar deformations since they are rigid and cannot occupy similar positions at the same time. The polymer being highly extensible and mobile is forced to undergo large variations in local strain. It is therefore not valid to assume the force contribution of each chain is similar, nor is it valid to assume the end-end displacements are small since very large strains can occur locally. Even small macroscopic strains can cause some fraction of the material to undergo very large local strains. For such conditions it is valid to assume that a chain will fail if some critical condition is exceeded. It is this type of localized failure that causes the "Mullins' Effect" in filled polymers. Such failure must preceed vacuole formation which is common in filled polymers. This behavior can be modeled for one dimensional behavior in a fairly general way by making the following assumptions [1]:

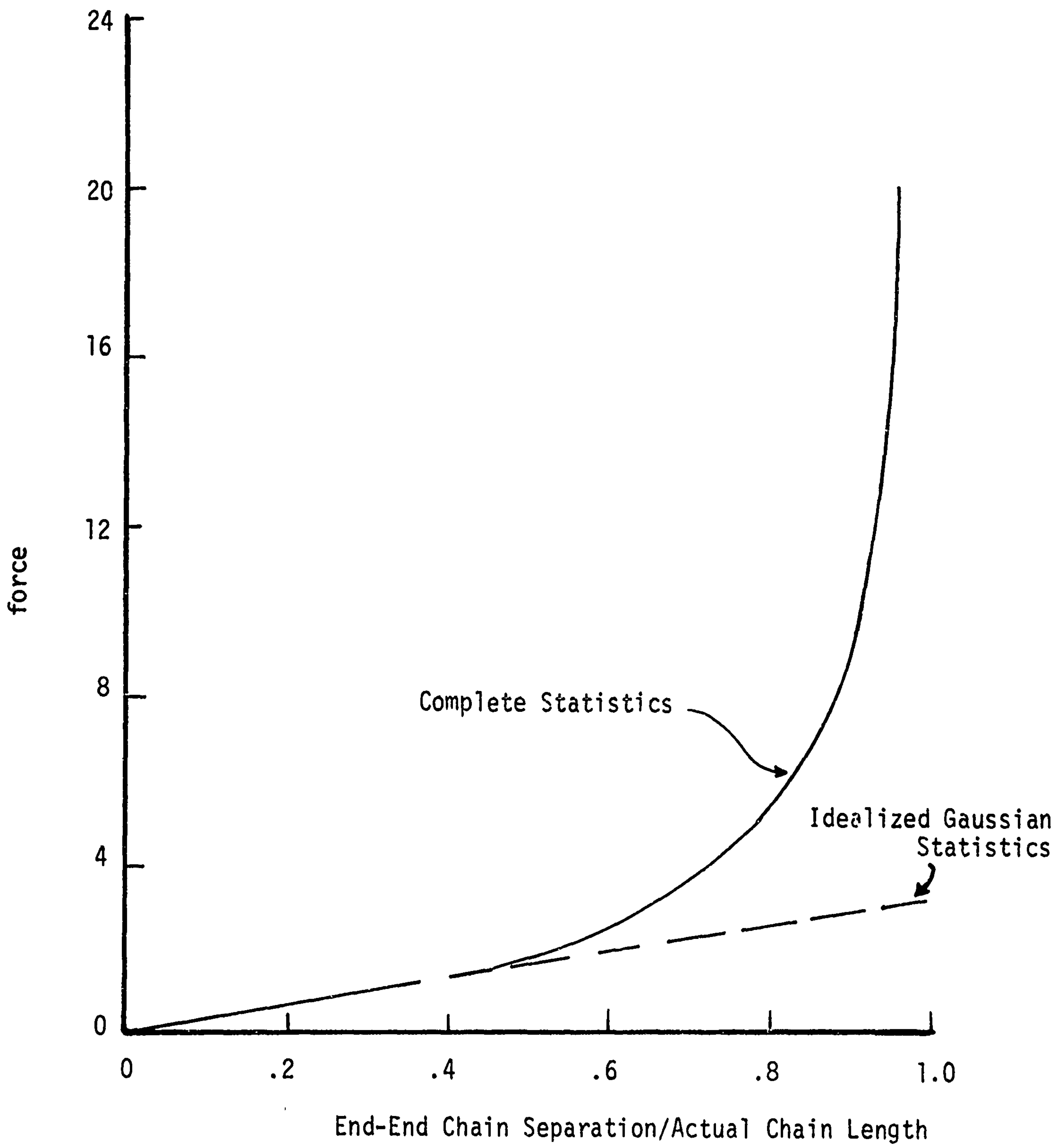


Figure 4.3 THE COMPLETE FORCE-EXTENSION RELATION FOR A RANDOM CHAIN COMPARED TO THE GAUSSIAN PREDICTION

1. The relative axial deformation of any given polymer chain is proportional to the axial applied strain, the proportionality constant differing from chain to chain.
2. Each polymer chain has the same elastic, but not necessarily linear, stress-strain law.
3. Each polymer chain fails and remains failed if at any time in its history some failure criterion is exceeded.

In these assumptions physically non-homogeneous local deformations, a non-linear stress-strain law for each element, and the possibility of having some of the elements fail have all been taken into account. Since the desired end result of this work is accurate constitutive relations for materials exhibiting permanent memory phenomenon that can be used in engineering analysis, emphasis will be placed on the behavior of elements, not necessarily on polymer chains. The resulting equations appear to be of value for describing many materials, not only amorphous polymers.

The first assumption can be expressed mathematically as

$$e_i(x_j, t) = e(t)\tau_i(x_j) \quad , \tag{4.1}$$

where e_i = axial strain in the i^{th} element

e = applied axial strain

τ_i = strain intensity factor for the i^{th} element

x_j = spatial coordinates

Assuming the elements are elastic and the problem strictly one dimensional and time independent, the failure criterion for an element can be expressed either as a maximum strain or maximum stress criterion. Assuming a chain fails when an extension e_{max} or equivalently stress s_{max} are exceeded, the following equation is obtained.

$$S_i = \begin{cases} f(e_i) = f(\tau_i e) & \text{if } \tau_i ||e|| \leq e_{max} \\ 0 & \text{if } \tau_i ||e|| > e_{max} \end{cases} \tag{4.2}$$

In equation (4.2) $f(e_i)$ is an arbitrary function that is single valued, and $||e||$ is the largest strain applied in the history of the deformation. The reason for using $||e||$ is it assures that once an element fails, it remains failed.

The observed stress from such a model is simply the total force divided by the total area which is given by

$$S = \frac{1}{A}\sum_{i=1}^{N} S_i = \frac{1}{A}\sum_{i=1}^{N} f(\tau_i e). \tag{4.3}$$

The summation in equation (4.3) can be more conveniently expressed as an integral. Using distribution theory equation (4.3) becomes

$$S = \int_0^{e_{max}/||e||} N(\tau) f(\tau e) d\tau \ . \tag{4.4}$$

In this integral $N(\tau)d\tau$ is a weighting function that represents the fraction of elements in a unit cross-section having strain intensity factors between τ and $\tau + d\tau$. The lower limit of integration can be taken as zero since $N(\tau)$ can be zero until some lower limit of τ is reached. The upper limit of integration is a function of the deformation history. The resulting stress-strain equation is a function of two variables, the current strain e, and the maximum strain in the deformation history, $||e||$. Before proceeding further, it should be pointed out that this simple stress-strain law can contain reversible as well as irreversible elastic responses which can be both linear and non-linear, up to and including failure by proper selection of the function $N(\tau)$. For example if all elements had the same intensity factor (e.g., rubber elasticity where $\tau_i = 1$) we obtain $N(\tau) = \delta(\tau-1)$, where δ is the Dirac delta function. The resulting integration yields

$$S = \begin{cases} f(e) & \text{if } ||e|| \leq e_{max} \\ 0 & \text{if } ||e|| > e_{max} \end{cases} \tag{4.5}$$

Similarly reversible behavior for only some small region of strain can be obtained by having $N(\tau)$ non-zero only for the same range of τ. An example of this case would be

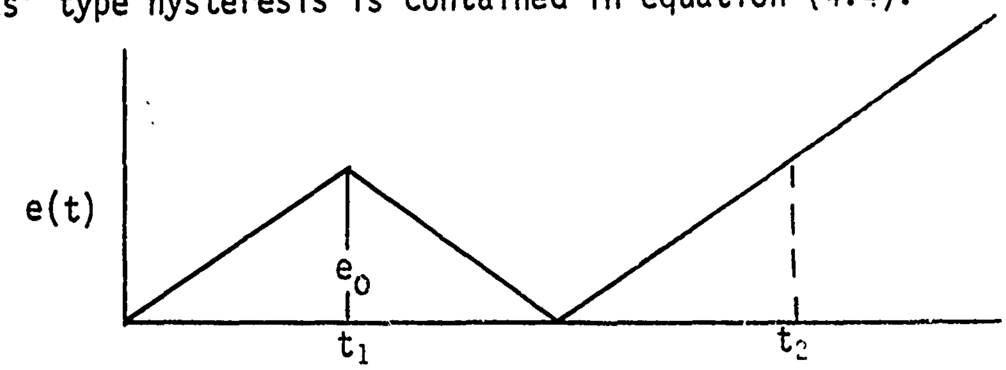
$$N(\tau) = \begin{cases} g(\tau) & \tau \leq a \\ 0 & \tau > a\ . \end{cases} \tag{4.6}$$

The resulting integration yields

$$S = \int_0^{e_{max}/||e||} N(\tau)f(\tau e)d\tau = \int_0^a g(\tau)f(\tau e)d\tau = f'(a,e)$$

$$\text{when} \quad a||e|| < e_{max} \; . \tag{4.7}$$

The problem at hand is not reversible behavior, but instead is irreversible phenomenon such as the "Mullins' Effect". Consider that $N(\tau)$ and $f(\tau e)$ are arbitrary but non-zero, and the material was subjected to the strain history given below, it can be shown that the Mullins' type hysteresis is contained in equation (4.4).



One cycle-stretch to failure strain input.

Since $||e||$ is by definition the maximum strain experienced in the deformation history, this input yields

$$||e|| = \begin{cases} e(t) & \text{if } 0 \leq t \leq t_1 \\ e_o & \text{if } t_1 \leq t \leq t_2 \\ e(t) & \text{if } t_2 \leq t \quad . \end{cases} \tag{4.8}$$

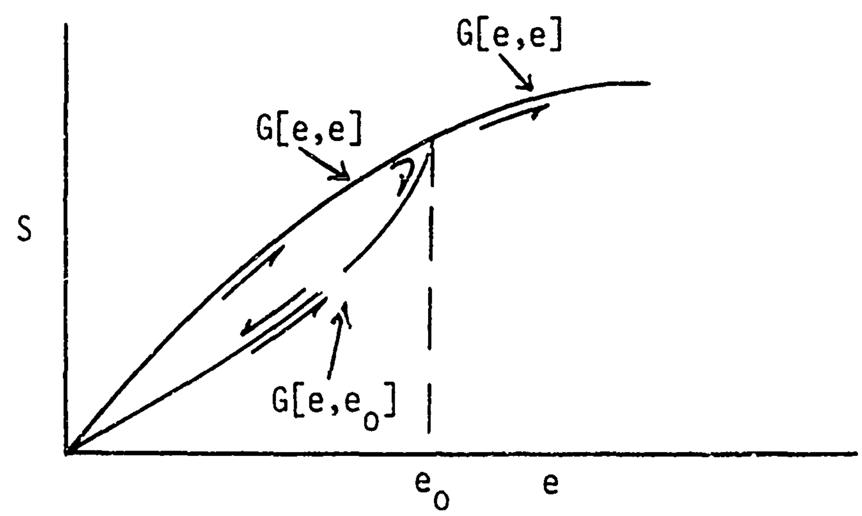
The resulting stress output for this case, when the values of range from zero to infinity would be

$$S(t) = \int_0^{e_{max}/e(t)} N(\tau)f(\tau e)d\tau = G[e(t),e(t)] \quad \text{if } 0 \le t \le t_1, \qquad (4.8a)$$

$$S(t) = \int_0^{e_{max}/e_0} N(\tau)f(\tau e)d\tau = G[e(t),e_0] \quad \text{if } t_1 \le t \le t_2, \qquad (4.8b)$$

$$S(t) = \int_0^{e_{max}/e(t)} N(\tau)f(\tau e)d\tau = G[e(t),e(t)] \quad \text{if } t_2 \le t \text{ .} \qquad (4.8c)$$

This type of behavior is illustrated in the sketch below.



Clearly equation (4.4) contains the Mullins' type hysterisis discussed earlier. Data from tests like the one illustrated above to increasing values of e_0 can be used to determine the distribution function $N(\tau)$ independent of the local stress-strain function $f(\tau e)$. Differentiating equation (4.8a) and (4.8b) with respect to strain,

subtracting one from the other, and evaluating each at $e = e_o$, produces

$$N(\tau = e_{max}/e_o) = \frac{C}{\tau^2} \left\{ G'[e,e_o] - G'[e,e] \right\}_{e=e_o} \tag{4.9}$$

$$\text{where } C = \frac{e_{max}}{f(e_{max})} = \text{constant} .$$

If for example the difference between these derivatives was found to be independent of e_o, then $N(\tau)$ would be proportional to $1/\tau^2$. For the general case the difference between these derivatives could be expanded in a polynomial in e_o to obtain

$$\left\{ G'[e_o,e] - G'[e,e] \right\}_{e=e_o} = \sum_{k=o}^{N} a_k e_o^k \tag{4.10}$$

$$\text{where } a_k = \text{constants}$$

The distribution function $N(\tau)$ could be determined as a polynomial in $1/\tau$ since in equation (4.9) the variable τ is evaluated at $\tau = e_{max}/e_o$. Substituting a polynomial for $N(\tau)$ and $f(\tau e)$ and performing the integration, the resulting equation for the stress output can be expressed as

$$S = A_1 e P_1(e/||e||) + A_2 e^2 P_2(e/||e||) + A_3 e^3 P_3(e/||e||) + \cdots,$$

$$\begin{aligned} \text{where } A_i &= \text{constants} \\ \text{and } P_i &= \text{polynomials in the variable } (e/||e||) \\ P_i(1) &= 1 \end{aligned} \tag{4.11}$$

There are only two possibilities for the variable $||e||$ in equation (4.11) or its predecessors, either $||e|| = e$ or $||e|| =$ constant. In the first case the unique stress-strain behavior for the first stretch is given. In the second case a hysteresis behavior dependent upon $||e||$ as well as e results.

4.2 Modeling the Irreversible Time Dependent "Mullins' Effect"

In the irreversible elastic case above a constitutive equation was derived that was dependent upon two variables, the current strain e, and the maximum strain in the history of the deformation, $||e||$. At first, one might think that by using the history dependent equation derived above as a multiplier to a hereditary type fading memory viscoelastic constitutive equation, an equation describing all the irregularities and non-linearities a filled polymer demonstrates could be obtained. This is not the case, and can be clearly demonstrated in a number of ways. The simplest proof is that for monotonically increasing strains $e = ||e||$, and the equation would contribute nothing new and no permanent memory phenomenon. Yet, filled polymers exhibit non-linearities of the type that cannot be handled by the Fréchet integral for such cases. Other features that must be contained in an accurate coupled constitutive equation is the concept of time dependent failure of elements and ultimately the material. These two possibilities clearly negate the possibility of so simple an equation of state.

There are two likely possibilities for incorporating time dependent failures. The first is to apply a kinetic reaction rate theory to the elastic elements, [1,55] and the second is to apply a cumulative damage law [45,54] to the elastic elements. The first of these approaches is inconsistent with the time independent case and leads to very cumbersome mathematics [1]. The cumulative damage concept on the other hand appears to be a natural extension of the time independent case since it contains equation (4.4) as a special case. It is this type of model that will be pursued here.

Linear cumulative damage theory based on Miners' law [1,54] requires that

$$D(t) = \sum_{k=1}^{M} (t_k/t_{fk}) \ . \tag{4.12}$$

In the above equation t_k is the time the material is held in the k^{th} state of stress or strain, t_{fk} is the time to failure for the material if this k^{th} state of stress or strain were acting alone, and $D(t)$ is the measure of damage. For such a theory, failure occurs when $D(t) = 1$. Since the elements of our model are elastic, it makes no difference if a stress or strain damage formulation is assumed. It simplifies the mathematics however if a strain cumulative damage criterion is assumed since our model expresses stress in terms of the strain history.

Using a power law strain-time to failure relation [54] for the singly applied strain gives for the i^{th} element

$$t_{fk} = C|e_i|^{-P} , \tag{4.13}$$

where $|\quad|$ indicates absolute value or magnitude,

and P = material property,

C = constant,

the damage equation becomes

$$CD_i(t) = \sum_{k=1}^{M} t_k|e_i|^P . \tag{4.14}$$

Equation (4.14) like equation (4.3) can be more conveniently expressed as the integral

$$CD_i(t) = \int_0^t |e_i(\xi)|^P d\xi, \quad \text{where } \xi = \text{dummy time.} \tag{4.15}$$

Recalling the e_i is the local strain in the i^{th} element and that this strain is related to the applied strain by τe, the equation for the stress becomes

$$S(t) = \int_0^{\tau_c(t)} N(\tau)f(\tau e)d\tau, \tag{4.16}$$

where τ_c = maximum permissible value of τ, and

$$\tau(t) = \left\{CD_i(t) \Big/ \int_0^t |e(\xi)|^P d\xi\right\}^{1/p} . \tag{4.17}$$

The maximum permissible value of τ, can be obtained by maximizing the numerator and minimizing the denominator in equation (4.17), or equivalently answering the question, what must the intensity factor τ on an element be such that its time to failure is the current time t? Upon setting $D_i(t) = 1$, equation (4.17) becomes

$$\tau_c(t) = C' \Big/ \left\{ \int_0^t |e(\xi)|^p d\xi \right\}^{1/p} = C'/||e||_p \qquad (4.18)$$

where C' = constant

Mathematically the quantity $||e||_p$ is called the p^{th} order Lebesgue norm [20,21] L^p. The L^p norm has properties that are worth noting and these are listed below.

$$||f||_p = \left\{ \int_0^t |f(\xi)|^p d\xi \right\}^{1/p}$$

a) $||af||_p = |a| \, ||f||_p$

b) $||f+g||_p \leq ||f||_p + ||g||_p$

c) $||fg||_1 \leq ||f||_p ||g||_p$

d) $||f-h||_p \leq ||f-g||_p + ||g-h||_p$

e) $||f||_\infty = \lim_{p\to\infty} \left\{ \int_0^t |f(\xi)|^p d\xi \right\}^{1/p} = \text{Maximum}_{0}^{t} \; |f(\xi)|.$

In the above equations f, g, and h are time functions, p and a are scalars, and ξ is a dummy time.

Thus for the time dependent case with permanent hysteresis our stress-strain equation becomes

$$S(t) = \int_0^{c'/||e||_p} N(\tau) f(\tau e) d\tau \ . \tag{4.19}$$

If $N(\tau)$ is non-zero in the range $0 \leq \tau < \infty$, then it can be expanded as suggested by equation (4.9) and (4.10). If $f(\tau e)$ is similarly expanded in a polynomial a form similar to equation (4.11) is obtained, the only difference being the replacement of $||e||$, which was defined as what is now known to be $||e||_\infty$, by $||e||_p$. The resulting stress-strain equation is

$$S(t) = A_1 e P_1(e/||e||_p) + A_2 e^2 P_2(e/||e||_p) + A_3 e^3 P_3(e/||e||_p) + \cdots, \tag{4.20}$$

where A_i = constants

P_i = polynomials in the variables $(e/||e||_p)$.

The use of p^{th} order Lebesgue norms in the constitutive equations is not original to this thesis. Fitzgerald [58] has proposed a constitutive equation wherein the stress is a functional of the present value of the deformation gradient and its p^{th} order Lebesgue norm. Coleman, Noll and Mizel have also proposed using these norms as approximations to the constitutive functionals [21,60]. Certain restricted forms of the constitutive equations developed in this study can be shown to be contained in these earlier works. The development

herein however was not motivated by the earlier works which were developed from a pure mathematical continuum approach. Instead the development in this dissertation stems from attempting to mathematically model the microstructural behavior of highly filled polymeric materials. Key variables, which were measures of microstructural damage, that were obtained from these models so happened to have the exact same mathematical definition as L^p norms and was brought to the author's attention by Fitzgerald. This work may therefore in some way physically justify the use of norms in constitutive theory.

It is clear that equation (4.19) and (4.20) contain the time independent behavior given by equations (4.4) and (4.11) as special cases by letting $p = \infty$.

In order to obtain equation (4.18) and therefore equations (4.20) and (4.21), it was assumed that t_{fk} in the cumulative damage relations was given by a simple power law. Equivalently this meant that the damage relation, $D(t)$, for this special case could be expressed in terms of the L^p norm as

$$[D_i(t)]^{1/p} = a||e_i||_p = D_i'(t) \ , \qquad (4.21)$$

where a is a constant and $D_i'(t)$ is some new measure of damage. Since failure was defined to occur when $D_i(t) = 1$, failure also occurs when $D_i'(t) = 1$ for all p. Although $D_i'(t)$ is a non-linear damage measure whenever $D(t)$ is linear, it has more useful properties than $D(t)$. An example of this is that by using equation (4.21) instead of equation (4.12) for this simple power law case, the strain cumulative damage

criterion contains the maximum strain failure criterion simply by letting $p = \infty$. Also equation (4.21) and equation (4.12) predict precisely the same time to failure for all arbitrary strain histories providing t_{fk} is given by a simple power law. Since any monotonically increasing function can be approximated in terms of L^p norms, cases when t_{fk} is not a simple power law can also be handled. Consider the case when $D_i'(t)$ can be given by

$$D_i'(t) = a_1||e_i||_1 + a_2||e_i||_2 + \cdots + a_p||e_i||_p. \quad (4.22)$$

For a simple step strain of magnitude e_{io}, the time to failure, t_f, is given by the equation

$$e_{io}^{-1} = a_1 t_f + a_2 t_f^{1/2} + \cdots + a_p t_f^{1/p} , \quad (4.23)$$

Letting $e_i = \tau e$ as before the critical value of τ at any time t becomes

$$\tau_c(t)^{-1} = a_1||e||_2 + a_2||e||_2 + \cdots + a_p||e||_p. \quad (4.24)$$

Equation (4.24) could be used to give the upper limit of integration in equation (4.16) and equations similar to equation (4.20) could be generated. This approach is not necessary since in the next section the approach given here is generalized to obtain three dimensional constitutive equations with permanent memory phenomenon. The importance

of the model approach selected is to shed light on key variables or measures to use in the constitutive equations.

Before proceeding further it would be wise to point out some of the behaviors possible using equation (4.19) or (4.20). Earlier in this thesis existing integral viscoelastic constitutive theories were criticized as being of limited value since they did not contain the special case of a homogeneous non-linear constitutive equation of degree one. Equation (4.19) clearly satisfies the concept of a simple material since if the history of the strain is known, the stress can be computed. To see if the homogeneity condition can be satisfied, the history $ae(\tau)$ is substituted for the history $e(\tau)$ and the two equations can be compared. Doing so we find after using the properties of L^p norms given above that

$$F[ae(\overset{t}{\underset{0}{\xi}})] = \int_0^{C'/|a|\,||e||_p} N(\tau)f(a\tau e)d\tau \ . \tag{4.25}$$

For the homogeneity condition to hold we must require for all $e(\overset{t}{\underset{0}{\xi}})$ and all scalars a

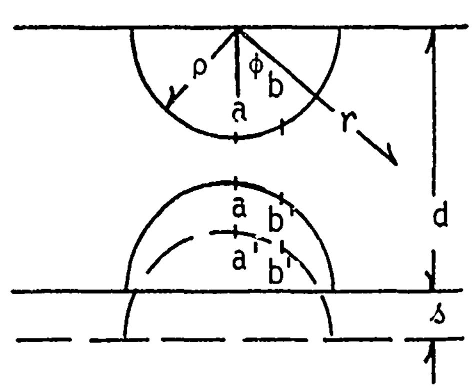
$$a\int_0^{C'/||e||_p} N(\tau)f(\tau e)d\tau = \int_0^{C'/|a|\,||e||_p} N(\tau)f(a\tau e)d\tau \ . \tag{4.26}$$

Replacing the dummy variable τ in the left hand side of equation (4.26) by $a\tau$, equation (4.26) becomes

$$a^2\int_0^{C'/a||e||_p} N(a\tau)f(a\tau e)d\tau = \int_0^{C'/|a|\,||e||_p} N(\tau)f(a\tau e)d\tau \ . \tag{4.27}$$

Observe that if $a^2N(a\tau) = N(\tau)$ and if the indefinite integral involves only even powers of τ, then the homogeneity condition will be satisfied. Note that $N(\tau) \approx 1/\tau^2$ meets the first requirement and the second requirement is satisfied simply by making the function f odd.

Before generalizing this method it should be shown that $N(\tau) \approx 1/\tau^2$ is representative of filled systems. This conclusion can be readily demonstrated by examining the distribution of effective gage lengths between two particles in a filled system. Recalling that $N(\tau)$ was the fraction of elements in a unit cross-section having intensity factors between τ and $\tau + d\tau$, the proof proceeds as follows. Consider, for simplicity's sake, an array of evenly spaced, rigid spherical particles embedded in a polymer matrix. From symmetry conditions, only one cell from such an array must be analyzed. The cell selected below is adequate for this purpose and can be thought of as a cube with sides d, having protuding half-spheres from the upper and lower faces as sketched below.



If the material is deformed, the distance d can be thought of as increasing from d to d + δ. Observe that the relative deformation

between points $\overline{aa}$ is considerably different from that at $\overline{bb}$. Defining the local strain as being

$$e_i = (\overline{a_i a_i} - \overline{aa})/\overline{aa} \quad (4.28)$$

where $\overline{aa}, \overline{a_i a_i}$ re considered functions of r.

The spacing between similar points on adjacent particles before deformation becomes

$$\overline{aa} = \begin{cases} d & \text{if } r \geq \rho. \\ d-2\rho\cos\phi & \text{if } r \leq \rho, \end{cases} \quad (4.29)$$

and after deformation the spacing becomes

$$\overline{a_i a_i} = \overline{aa} + \delta. \quad (4.30)$$

The local strain in this one dimensional model is given by

$$e_i(r) = \begin{cases} \delta/d & \text{if } r \geq \rho \\ \delta/(d-2\rho\cos\phi) & \text{if } r \leq \rho. \end{cases} \quad (4.31)$$

The observable macroscopic strain e, for such a deformation would simply be δ/d.

Defining the intensity factor τ as being the ratio of local to measured strain, one obtains

$$\tau(r) = \frac{e_i(r)}{e} = \begin{cases} 1 & \text{if } r \geq \rho \\ (1-2\frac{\rho}{d}\cos\phi)^{-1} & \text{if } r \leq \rho. \end{cases} \tag{4.32}$$

The distributing function $N(\tau)$ can be found by integrating over the middle cross-section those elements having intensity factors τ. This computation may be carried out more easily by expressing the incremental cross-sectional area in terms of τ and ϕ. To accomplish this, note that those elements having constant τ are on a circle of constant r. The elemental strip of area is $2\pi r dr$, where $r = \rho\sin\phi$. The incremental strip of area can be expressed as

$$dA(\tau) = 2\pi\rho^2 \sin\phi\cos\phi\, d\phi \qquad \text{for } r \leq \rho \tag{4.33}$$

Differentiating equation (4.32) to obtain the value of $\sin\phi$ and solving equation (4.32) for the value of $\cos\phi$ equation (4.33) becomes

$$dA(\tau) = \frac{\pi d^2}{2}\left(\frac{1}{\tau^2} - \frac{1}{\tau^3}\right), \qquad r \leq \rho \tag{4.34}$$

Assuming the elements are distributed uniformly over the section, yields $N(\tau) \simeq dA(\tau)$. Accounting also for the portion where $r > \rho$ in which $\tau = 1$, completes the computation. The final relation for $N(\tau)$ from the simple model described above is

$$N(\tau) = (1-\pi(\rho/d)^2)\,\delta(\tau-1) + \frac{\pi}{2}\left(\frac{1}{\tau^2} - \frac{1}{\tau^3}\right),$$

$$\text{where } 1 \leq \tau \leq (1-2\rho/d)^{-1} \tag{4.35}$$

$\delta(\tau-1)$ = Dirac Delta Function.

The volume fraction of filler of this model system can be expressed in terms of the parameters ρ and d as $V_f = \frac{4\pi}{3}(\pi/d)^3$, where V_f is the volume fraction of filler in the composite model. The maximum value of τ therefore becomes

$$\tau_{max} = \left[1 - 2\left(\frac{3V_f}{4\pi}\right)^{1/3}\right]^{-1} \qquad (4.36)$$

Equation (4.36) indicates that as V_f increases even to modest values, τ_{max} becomes quite large and in fact approaches infinity for this simple model as $V_f \to 0.52$. Clearly when τ is large equation (4.35) becomes $N(\tau) \approx 1/\tau^2$. The main difference is that the lower limit of in the calculated distribution is 1 whereas in equation (4.19) it was taken as zero. In filled polymers exhibiting the "Mullins' Effect", this is of no concern, since the stress-strain behavior of an element is very non-linear as indicated by the Langevin statistic and nearly all of the stress is being supported only by a small fraction of the polymer chains. Equation (4.19) can contain the types of behavior exhibited by solid propellants and other filled polymers and also the forms $N(\tau)$ and $f(\tau\varepsilon)$ must take on are consistent with propellant microstructure.

Before proceeding further to the development of three dimensional constitutive equations, considerable insight into the problems of mechanical characterization of materials can be obtained by analyzing the simple one dimensional equation given in equations (4.19) and (4.20). To restrict this equation to homogeneous functionals of degree

one a sufficient condition is to require that equation (4.19) have the form

$$S(t) = A_1 eP\left((e/||e||_p)^2\right) . \tag{4.37}$$

In the above equation P is a polynomial in the variable $(e/||e||_p)^2$. This condition is necessary if scalar multiplication is to hold for all scalars, positive or negative. A special case of this equation is

$$S(t) = 100e[1 + (e/||e||_p)^n], \text{ where n is an even integer.} \tag{4.38}$$

Equation (4.38) gives a relaxation modulus that is independent of the applied strain magnitude, and will obey the homogeneity requirement of linearity for all scalars, with any arbitrary strain input. Equation 4.38 is not linear however as norms are not superposable except in the most trivial examples. The material represented by equation (4.38) is therefore non-linear, but for many types of tests used for material characterization it could not be distinguished from a linear viscoelastic material. In fact, the parameters n and P appearing in this constitutive equation can be adjusted so that the derivative of the constant strain rate test is proportional to the relaxation modulus; a commonly cited property of a linear viscoelastic material [19,45]. Careful examination of the stress output to various strain inputs confirms the non-linear nature of this equation and

indicate it is within the range of this simple equation to describe the one-dimensional response of solid propellants at small strains. To demonstrate this ability, the stress output for a variety of strain inputs have been determined for different values of n and P.

These data are illustrated in figure 4.4 through 4.9. In these calculations the ratio n/P has been kept constant; therefore all of the materials would exhibit the same relaxation modulus. However as clearly indicated by these figures, the behavior to other inputs is different for the different values of n and P. This feature of giving the same output for one test, yet a different output for other tests, is characteristic of non-linear systems. If the material were linear, this feature would be impossible since one test dictates the results of all other tests for linear systems. Characterization of non-linear materials is therefore a difficult task as many tests must be used. Individuals familiar with the behavior of linear viscoelastic materials and the non-linear behavior of composite solid propellants will observe great similarity between the data illustrated in figures 4.4 through 4.9 and the behavior of these materials.

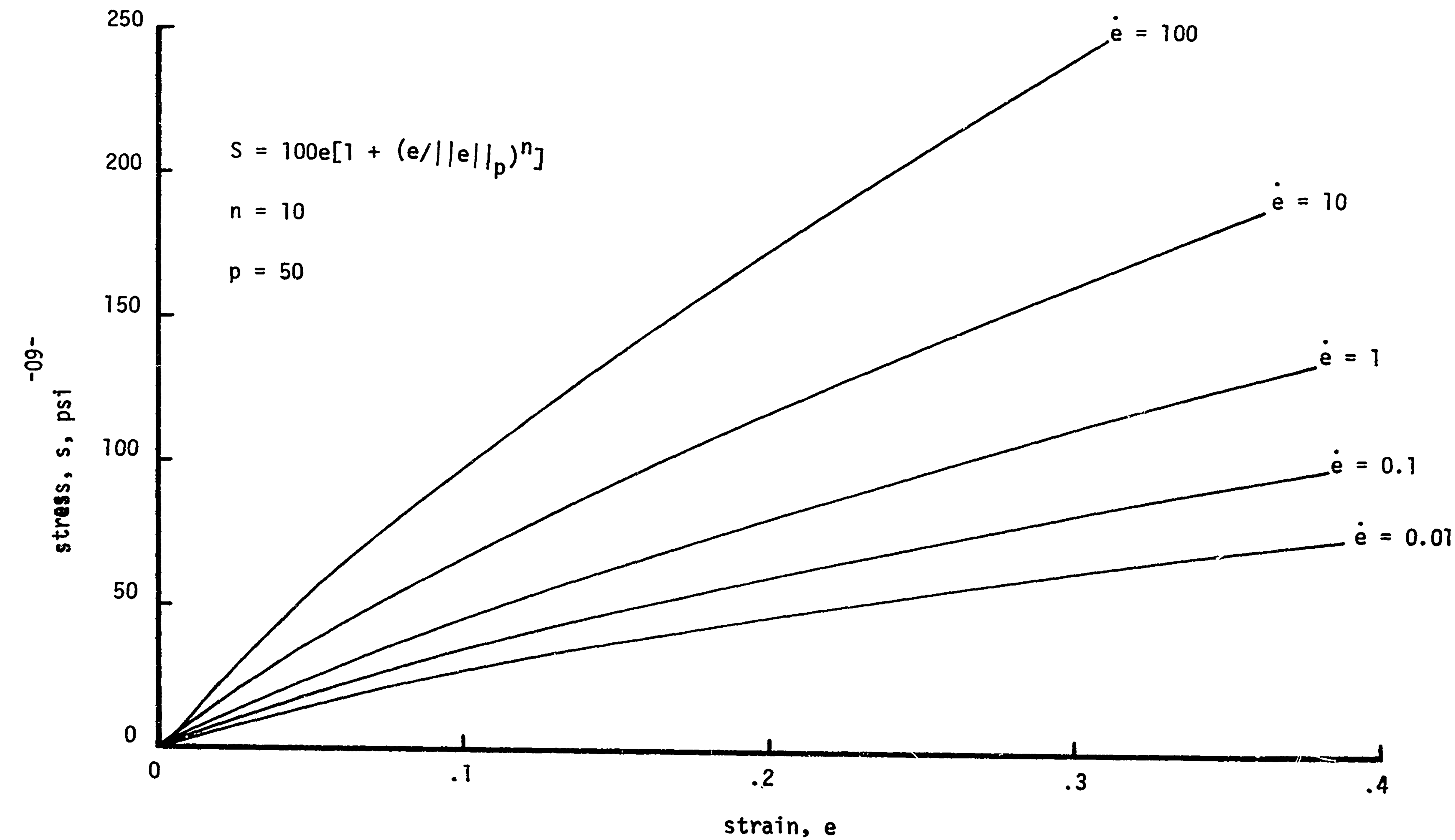


Figure 4.4 CALCULATED CONSTANT RATE STRESS-STRAIN BEHAVIOR OF A PERMANENT MEMORY MATERIAL.

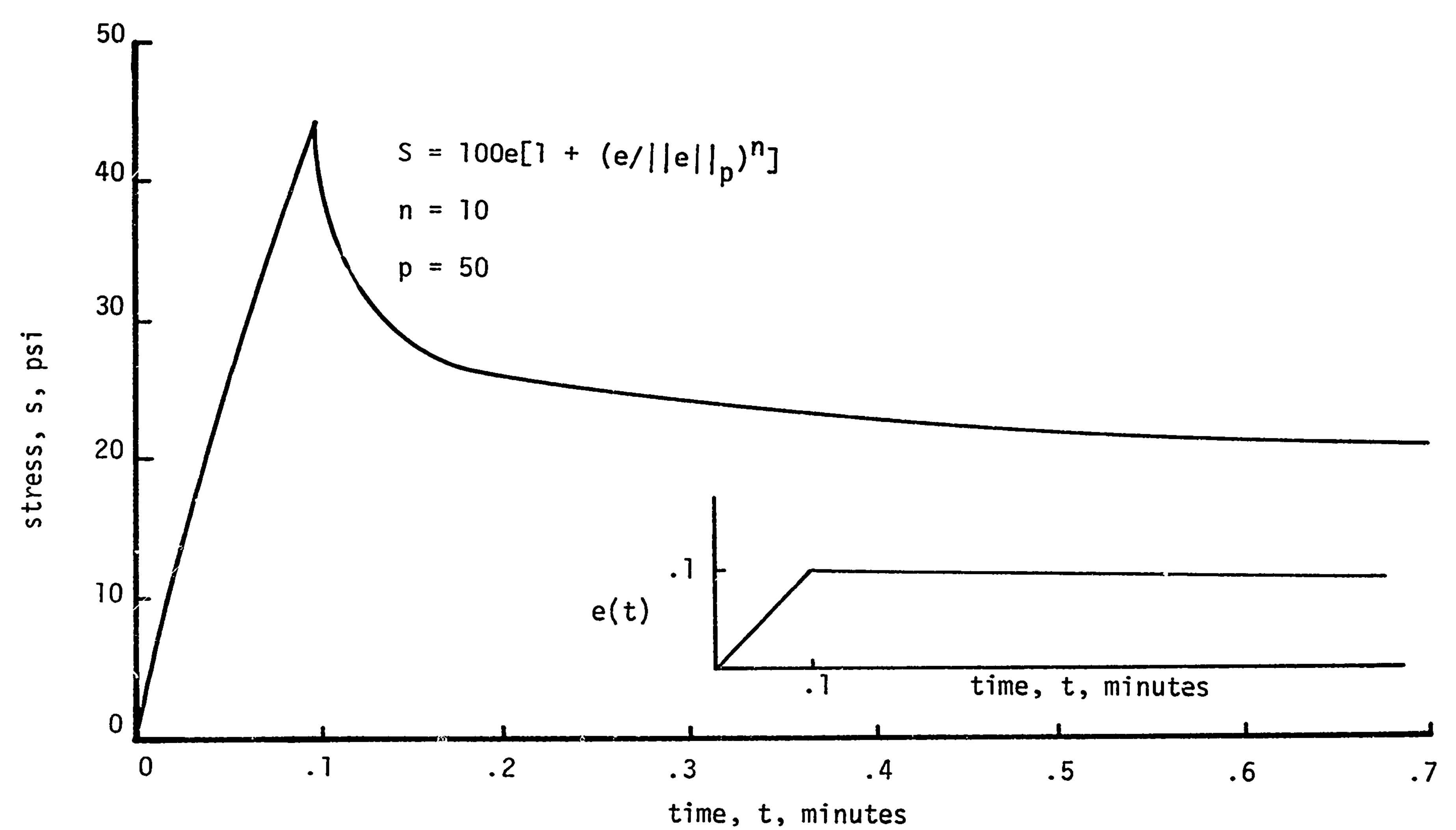


Figure 4.5. CALCULATED RAMP STRAIN STRESS RELAXATION BEHAVIOR OF A PERMANENT MEMORY MATERIAL.

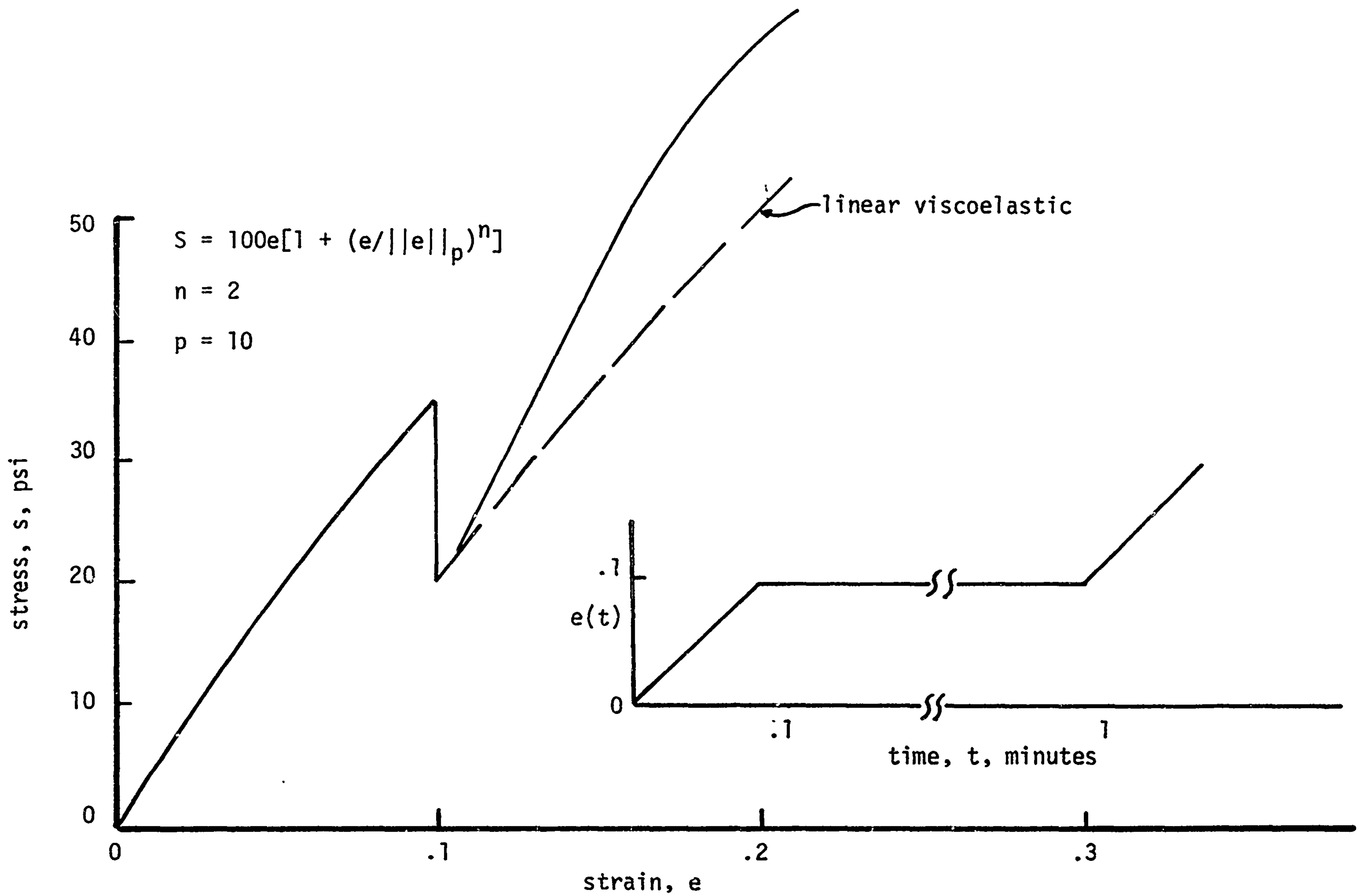


Figure 4.6. CALCULATED PERMANENT MEMORY STRESS-STRAIN RESPONSE TO AN INTERRUPTED RAMP INPUT.

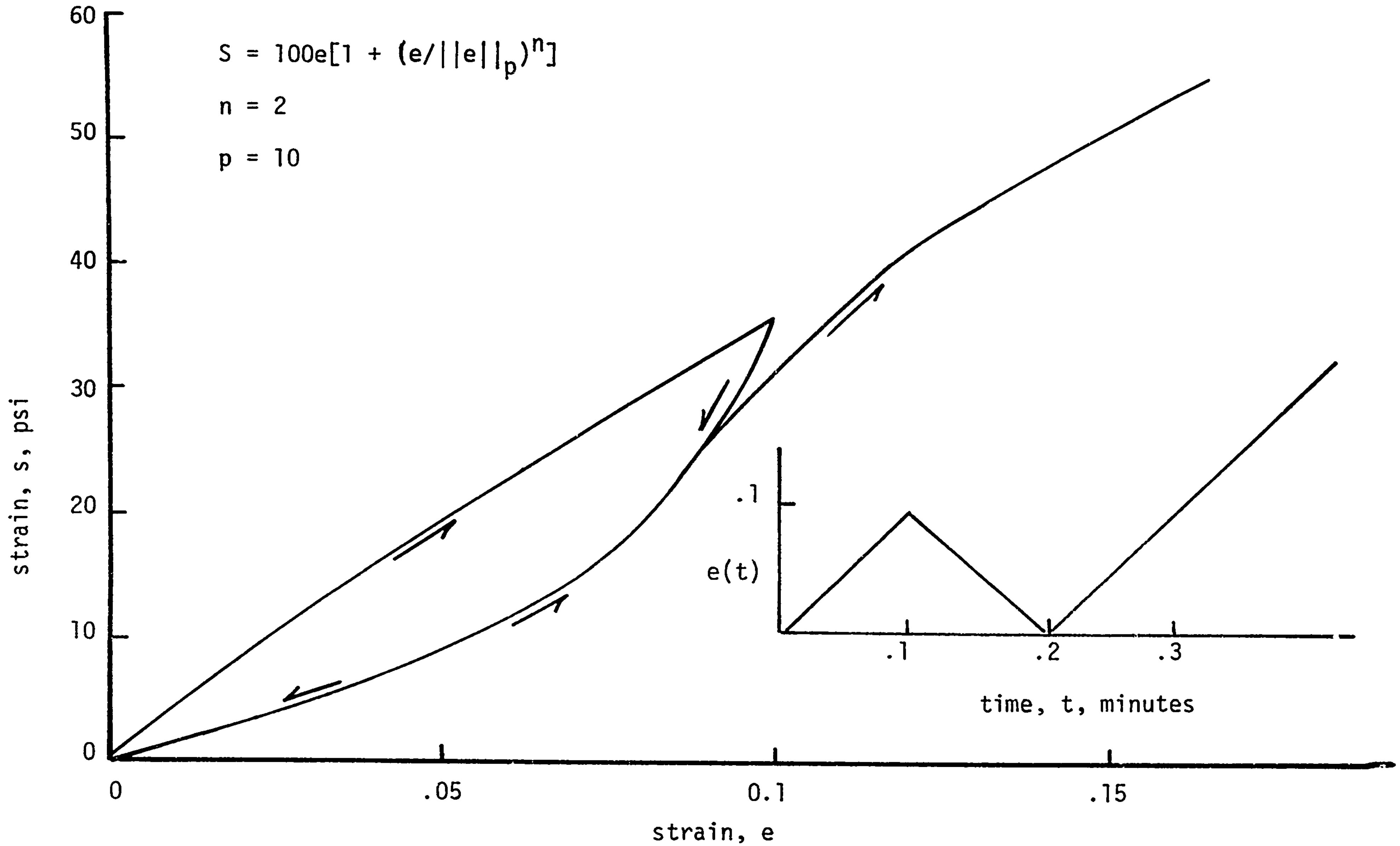


Figure 4.7. CALCULATED PERMANENT MEMORY HYSTERESIS RESPONSE TO A REVERSED RAMP-STRAIN INPUT.

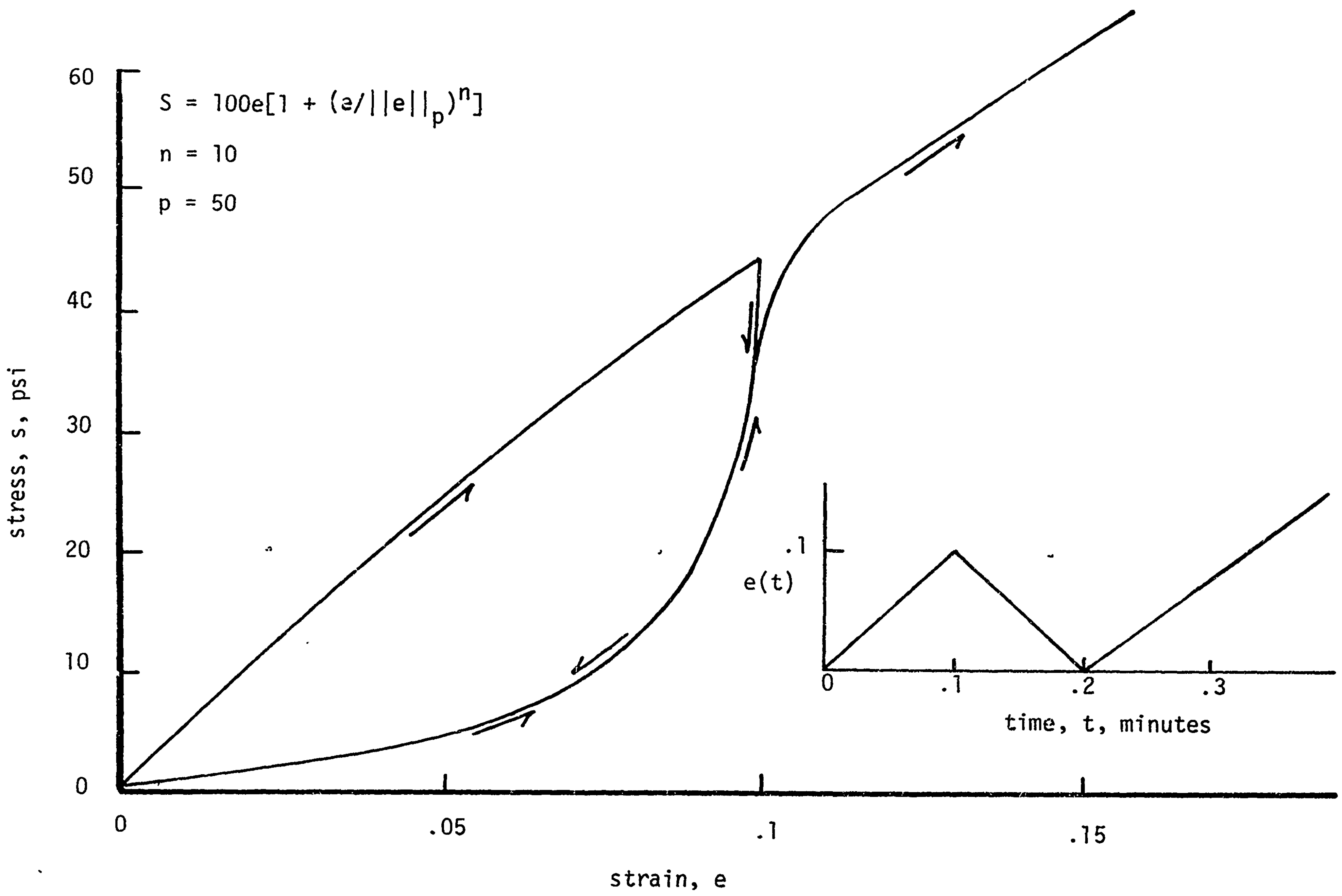


Figure 4.8. CALCULATED PERMANENT MEMORY HYSTERESIS RESPONSE TO A REVERSED RAMP STRAIN INPUT.

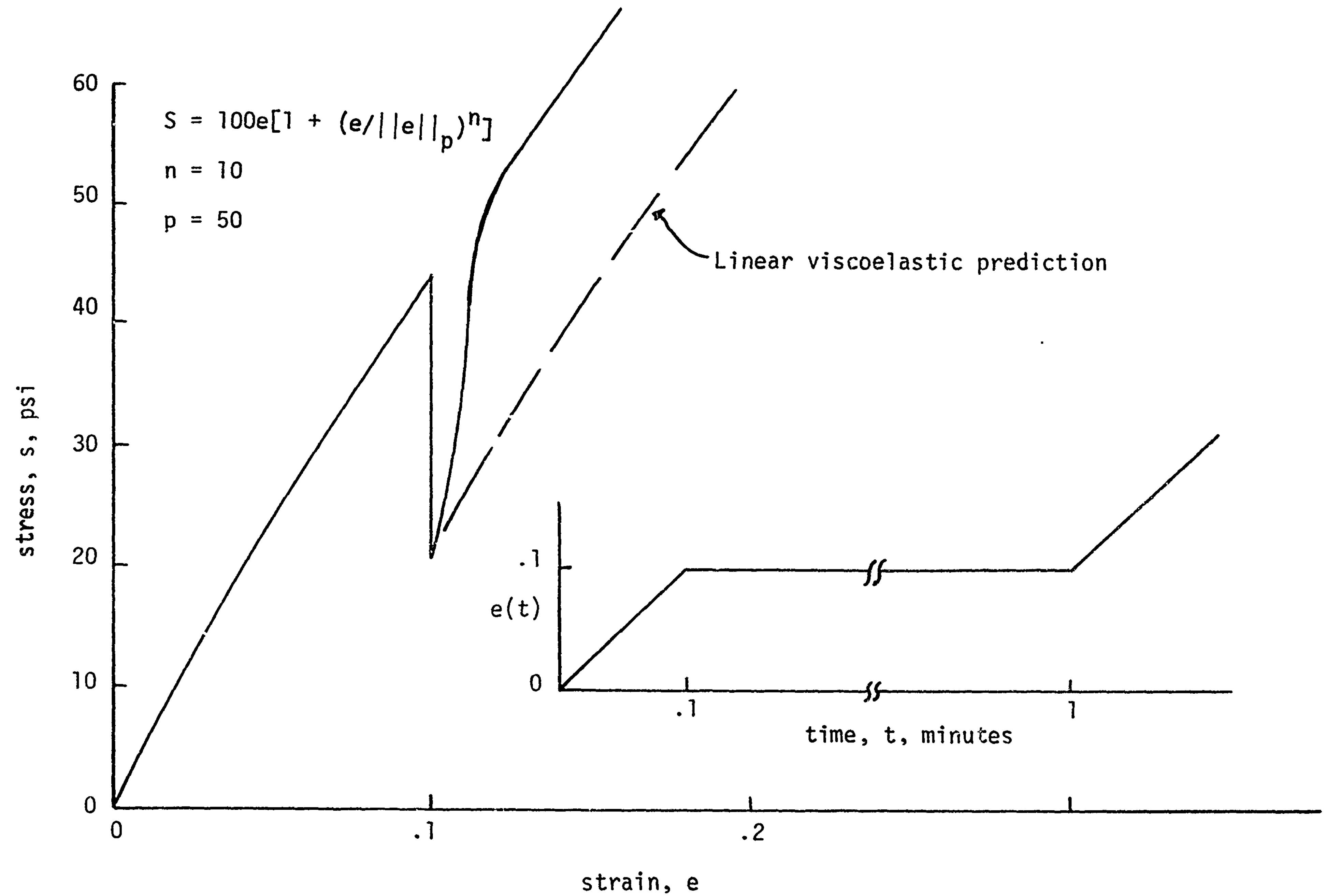


Figure 4.9. CALCULATED PERMANENT MEMORY STRESS-STRAIN RESPONSE TO AN INTERRUPTED RAMP INPUT.

V. THREE DIMENSIONAL CONSTITUTIVE EQUATIONS

In section 3 it has been demonstrated that the Fréchet expansion provides a constitutive equation that is of little value for materials with non-linear homogeneous constitutive equations. In order to develop a general non-linear constitutive equation with homogeneity of degree one, the restrictions imposed by this expansion must be circumvented. The main difficulty lies in the fact that the Fréchet multiple integral expansion represents a time-memory mechanism. In section 4 it was demonstrated that if the so called L^P norms of the deformation history could appear in the constitutive equation, then many of these difficulties could be eliminated. It should be pointed out that the L^P norms yield a strain-memory mechanism and not just a time-memory mechanism. This section will primarily deal with constitutive equations for non-linear materials having homogeneous constitutive equations of degree one that can describe the mechanical response of solid propellants and are amenable to three dimensional stress analysis.

The simplest way to proceed in the development of constitutive equations homogeneous to degree one is to recall the stress-strain equation for isotropic materials given by Green and Rivlin was

$$\underline{S}(t) = K_0(t)\underline{I} + \int_0^t K_1(t,\tau_1)\underline{\dot{e}}(\tau_1)d\tau_1 + \int_0^t\int_0^t K_1(t,\tau_1,\tau_2)\underline{\dot{e}}(\tau_1)\underline{\dot{e}}(\tau_2)d\tau_1 d\tau_2 + \cdots + \int_0^t \cdots \int_0^t K_n(t,\tau_1,\cdots,\tau_n)\underline{\dot{e}}(\tau_1)\cdots\underline{\dot{e}}(\tau_n)d\tau_1\cdots d\tau_n + \cdots, \quad (5.1)$$

where $K_n(t,\tau_1,\tau_2,\cdots\tau_n) = K_n\left[\overset{t}{\underset{o}{I_1(\xi)}},\overset{t}{\underset{o}{I_2(\xi)}},\overset{t}{\underset{o}{I_3(\xi)}},t,\tau_1,\cdots\tau_n\right]$,

and ξ = dummy time*. (5.1 con't)

In this theory the kernels were functionals of the history of the scalar invariants of the Cauchy infinitesimal strain tensor as well as the generic and current values of time. If the form of these kernel functionals was given again as a Fréchet expansion, then the class of materials having non-linear homogeneous constitutive equations was shown not to be contained by the theory. There is great similarity between equation (5.1) and the one dimensional irreversible equation obtained from the models in section 4, which was given as

$$S = A_1eP_1(e/||e||_p) + A_2e^2P_2(e/||e||_p) + A_3e^3P_3(e/||e||_p) + \cdots$$

$$+ A_ne^nP_n(e/||e||_p) + \cdots \quad (5.2)$$

Equation (5.2) allows for no fading memory viscoelasticity, only permanent strain-time memory. If the kernel functionals of equation (5.1) were allowed to take on terms like $(||I_1||_p/||I_1||_q)$, then the equation could contain two types of memory phenomenon; the fading memory viscoelasticity contained in the hereditary integral representation and the permanent memory behavior registered in the L^P norms.

*The dummy time ξ is introduced so that no confusion can arise as to what variables enter into the integration process.

It is important to note here that none of the principles of isothermal continuum mechanics are being violated. The only principle that could be violated is that of objectivity which states the constitutive equation should remain invariant to an arbitrary rotation or translation of our reference frame [25,26,27]. If the strain measure itself is objective and the stress written as a functional of the objective measure, then the constitutive equation will automatically be objective as shown by Green and Rivlin [29].

Before proceeding in the development of homogeneous constitutive equations of degree one, a special case of equation (5.1) is worth mentioning. Note that when the kernel functionals are independent of the variables τ_i, $i = 1,\cdots n$, then the integrations can be performed and the result is

$$\underline{S}(t) = K_0(t)\underline{I} + K_1(t)\underline{e}(t) + K_2(t)\underline{e}^2(t) + \cdots + K_n(t)\underline{e}^n(t) + \cdots ,$$

$$\text{where } K_i(t) = K_i\left[\overset{t}{\underset{0}{I_1(\xi)}}, \overset{t}{\underset{0}{I_2(\xi)}}, \overset{t}{\underset{0}{I_3(\xi)}},\ t\right]. \tag{5.3}$$

Applying the Cayley-Hamilton theorem [25,27,30], equations (5.3) can be reduced to the form

$$\underline{S}(t) = \psi_0\underline{I} + \psi_1\underline{e}(t) + \psi_2\underline{e}^2(t) \quad ,$$

$$\text{where } \psi_i = \psi_i\left[\overset{t}{\underset{0}{I_1(\xi)}}, \overset{t}{\underset{0}{I_2(\xi)}}, \overset{t}{\underset{0}{I_3(\xi)}}, I_1(t), I_2(t), I_3(t), t\right]. \tag{5.4}$$

Equation (5.4) represents a viscoelastic material where all the time effects come from the history of the scalar invariants of strain and also from aging effects, which can be eliminated by removing the variable t. Depending on the form of the functionals ψ_i, this particular constitutive equation can describe both permanent and fading memory viscoelasticity with strain coupling. When the history dependence is eliminated from the functionals ψ_i, then equation (5.4) reduces to equation (3.20), the standard non-linear elastic equation for isotropic materials.

The development of constitutive equations which are homogeneous to degree one is quite simple and can be done by simply imposing restrictions or constraints on equation (5.1). Recall homogeneity of degree one simply means that scalar multiplication is valid for all scalars. Recall also that the strain invariants are given by

$$I_1 = e_{11} + e_{22} + e_{33}$$

$$I_2 = e_{11}e_{22} + e_{11}e_{33} + e_{22}e_{33} - e_{12}^2 - e_{13}^2 - e_{23}^2$$

$$I_3 = e_{11}e_{22}e_{33} + 2e_{12}e_{13}e_{23} - e_{11}e_{23}^2 - e_{22}e_{13}^2 - e_{33}e_{12}^2 \quad (5.5)$$

Mathematically the homogeneous constitutive equation of degree one has the property that the equation

$$F_{ij}\left[a e_{pq}\left(\overset{t}{\underset{\tau=0}{t,\tau}}\right)\right] = aF_{ij}\left[e_{pq}\left(\overset{t}{\underset{\tau=0}{t,\tau}}\right)\right] \quad (5.6)$$

holds for all real scalars, all strain inputs and all time t. Since the first strain invariant is homogeneous to degree one, the second to degree two, and the third to degree three, non-linear homogeneous constitutive functionals can be constructed within the framework of the Green-Rivlin theory.

From physical reasoning kernel functionals homogeneous to degree less than zero cannot be admitted since they can yield unbounded stresses or singularities which are not real. With this added restriction the most general constitutive equation homogeneous to degree one within the range of applicability of equation (5.1) is

$$S_{ij}(t) = \delta_{ij} \int_0^t K_0\left[\overset{t}{\underset{0}{I_1(\xi)}}, \overset{t}{\underset{0}{I_2(\xi)}}, \overset{t}{\underset{0}{I_3(\xi)}}, t, \tau\right] \dot{e}_{kk}(\tau)d\tau$$

$$+ \int_0^t K_1\left[\overset{t}{\underset{0}{I_1(\xi)}}, \overset{t}{\underset{0}{I_2(\xi)}}, \overset{t}{\underset{0}{I_3(\xi)}}, t, \tau\right] \dot{e}_{ij}(\xi)d\tau ,$$

where $K_i\left[a\overset{t}{\underset{0}{I_1(\xi)}}, a^2\overset{t}{\underset{0}{I_2(\xi)}}, a^3\overset{t}{\underset{0}{I_3(\xi)}}, t, \tau\right] =$

$$K_i\left[\overset{t}{\underset{0}{I_1(\xi)}}, \overset{t}{\underset{0}{I_2(\xi)}}, \overset{t}{\underset{0}{I_3(\xi)}}, t, \tau\right]. \tag{5.7}$$

In equation (5.7) the kernel functionals are homogeneous to degree zero. If the kernels are independent of the history of the invariants then the equation reduces to that of linear viscoelasticity. If the material is non-aging, equation (5.7) must reduce to [28,29]

$$S_{ij}(t) = \delta_{ij} \int_0^t K_0\left[I_1(\overset{t}{\underset{0}{\xi}}), I_2(\overset{t}{\underset{0}{\xi}}), I_3(\overset{t}{\underset{0}{\xi}}), t-\tau\right]\dot{e}_{kk}(\tau)d\tau$$

$$+ \int_0^t K_1\left[I_1(\overset{t}{\underset{0}{\xi}}), I_2(\overset{t}{\underset{0}{\xi}}), I_3(\overset{t}{\underset{0}{\xi}}), t-\tau\right]\dot{e}_{ij}(\tau)d\tau \ . \tag{5.8}$$

In a similar manner the state of strain can be expressed in terms of the history of the stresses for homogeneous equations of degree one as

$$e_{ij}(t) = \delta_{ij} \int_0^t L_0\left[J_1(\overset{t}{\underset{0}{\xi}}), J_2(\overset{t}{\underset{0}{\xi}}), J_3(\overset{t}{\underset{0}{\xi}}), t-\tau\right]\dot{S}_{kk}(\tau)d\tau$$

$$+ \int_0^t L_1\left[J_1(\overset{t}{\underset{0}{\xi}}), J_2(\overset{t}{\underset{0}{\xi}}), J_3(\overset{t}{\underset{0}{\xi}}), t-\tau\right]\dot{S}_{ij}(\tau)d\tau \ , \tag{5.9}$$

In equation (5.9) the J_i are the principle stress invariants, and the kernels have the property that

$$L_i\left[aJ_1(\overset{t}{\underset{0}{\xi}}), a^2J_2(\overset{t}{\underset{0}{\xi}}), a^3J_3(\overset{t}{\underset{0}{\xi}}), t-\tau\right] = L_i\left[J_1(\overset{t}{\underset{0}{\xi}}), J_2(\overset{t}{\underset{0}{\xi}}), J_3(\overset{t}{\underset{0}{\xi}}), t-\tau\right] \ . \tag{5.10}$$

Except for the case when the equations reduce to linear equations, direct inversion from equation (5.8) to equation (5.9) appears to be virtually impossible. Unlike the linear constitutive equations the power of Laplace transforms cannot be applied since these transforms can be applied only to linear functionals. This difficulty does not mean that the inversion does not exist. In fact the homogeneity

condition alone intuitively suggests that the inversion does exist since scalar multiplication must hold for all scalars and this type of one-to one behavior is characteristic of invertible systems. For the purpose of this thesis however, equation (5.9) is given as the inverse form of equation (5.8) when such an inverse exists.

VI. ANNIHILATORS, A TYPE OF FADING MEMORY

In section 4 a one dimensional permanent memory constitutive equation was developed using L^P norms as a history measure. In section 5 the constitutive equation of Green and Rivlin was extended to include homogeneous non-linear constitutive functionals of degree one. This extension simply placed general restrictions on the kernel functionals of the integral expansion representation and no particular forms for the kernel functionals were given. The final equations given in section 5 contain a type of permanent memory as well as fading memory elastic and viscoelastic behavior. The word elastic in this sense is being used in the classical definition [22,24,36] which states a material is elastic if it returns to its original shape when all the tractions are removed. Fading memory implies the material will also return to its original properties if allowed to rest sufficiently. If the material has both fading memory and permanent memory components that make up its total behavior, the combined response is naturally of the permanent memory type. Some materials exhibit a type of fading memory not contained in the conventional sense of fading memory. To illustrate this more clearly, a fading memory viscoelastic material will recover its original properties on essentially the time scale as it can dissipate energy. Often in the field of polymer rheology the measure relaxation times γ_i, or retardation times β_i, are used to characterize materials in Prony series type representations [19,61]. If a material has a single relaxation time γ, then it will recover its original properties when

the tractions are removed if it is allowed to rest for a time, say $\delta\gamma$. Materials exhibiting the "Mullins' Effect" often exhibit no relaxation or rate effects yet will recover all or some portion of their original properties if allowed to rest for very long periods of time [5,6,60]. This rehealing phenomenon, as it has often been called, implies the reversing of permanent damage or memory and occurs on a completely different time scale than any viscous effects. This behavior could be viewed as some form of annihilation of the permanent memory measures which are governing the materials response. The rehealing phenomenon is common in solid propellants and most filled polymer materials and must be properly accounted for in accurate constitutive equations for these materials.

The mathematical formulation of the rehealing phenomenon into the constitutive equations is not difficult, and in no way destroys the homogeneity restriction placed on the kernel functions in the latter part of section 5. There are numerous ways in which the rehealing phenomenon can be included. In section 4 it was shown that L^P norms were convenient and realistic measures of permanent memory phenomenon, therefore a more general norm will be defined which yields the behavior discussed above. In section 4 the norm $||f||_p$ was defined as

$$||f||_p = \left\{ \int_0^t |f(\xi)|^p d\xi \right\}^{1/p} \tag{6.1}$$

A weighted norm [20,21,60], $||f||_{h,p}$, is now defined as

$$||f||_{h,p} = \left\{ \int_0^t (|f(\xi)|\, h(t-\xi))^p d\xi \right\}^{1/p} , \qquad (6.2)$$

where $h(t-\xi)$ is a positive function which weights the function $f(\xi)$ over its history as ξ ranges from zero to t. For our purposes it is sufficient to define the weight function as

$$h(t-\xi) = \begin{cases} 1 & \text{if } \xi = t \\ \leq 1 & \text{if } \xi < t \end{cases} \qquad (6.3)$$

A logical choice for the weight function is a single exponential term or perhaps a Prony series. For the purposes of this thesis it is sufficient to demonstrate that the use of such a norm in the constitutive equation yields the rehealing behavior discussed earlier. Note that when the weight function is unity for all its arguments, then the conventional norm is recovered; use of $||f||_{h,p}$ norms in constitutive functionals contains those functionals only using $||f||_p$ norms.

As an example, consider the case when $h(t-\xi)$ is defined as a simple exponential term

$$h(t-\xi) = \exp(-b(t-\xi)) = \exp(-bt)\exp(b\xi) , \quad \text{where } b \geq 0 . \qquad (6.4)$$

The weighted norm now becomes

$$||f||_{h,p} = \exp(-bt) \left\{ \int_0^t |f(\xi)|^p \exp(bp\xi) d\xi \right\}^{1/p} . \qquad (6.5)$$

This weighted norm has some interesting properties that are discussed below which indicate it is within the capabilities of such norms to describe the properties discussed above with reference to the rehealing phenomena.

1) If the constant $b \ll P$, then the annihilation of memory will be on a completely different time scale than any relaxation phenomena. Hence for short times, the $||f||_{h,p}$ norm will behave approximately as the $||f||_p$ norm.

2) Total annihilation can only take place when the function $f(\xi)$ is returned to the rest state, $f = 0$, the annihilation then takes place at the rate $||f||_{h,p} \sim ce^{-b(t-t_0)}$ where $f(\xi) = 0$ when $\xi > t_0$.

3) If the function $f(\xi)$ is held constant, say at f_0, for some long time period, the accumulation and annihilation of the norm balance each other and a constant norm is achieved at long times.

$$||f_0||_{h,p} = \exp(-bt)\left\{\int_0^t |f_0|^p \exp(bP\xi)d\xi\right\}^{1/p} =$$

$$|f_0|\exp(-bt)\left[\frac{\exp(bPt)-1}{bP}\right]^{1/p} ,$$

or

$$||f_o||_{h,p} \rightarrow |f_o|(bP)^{-1/p} \text{ as } bt \rightarrow \text{large valucs.}$$

To demonstrate that in a constitutive equation the proper type of behavior can be obtained, consider the simple one dimensional constitutive equation of the form

$$S(t) = Ae(t)(||e||_{h,p}/||e||_{h,q}) ,$$

$$\text{where } h(t-\xi) = \exp(-bt)\exp(b\xi), \text{ and } p>q>>b . \quad (6.6)$$

For short times the equation behaves exactly as it would if unweighted norms were used. If a state of strain is held constant for sufficiently long times, the stress will decay to some equilibrium non-zero value directly proportional to the constant strain e_o. If allowed to recover in the rest state for some long period of time, some or all of the original response will be recovered. These effects are shown in figures 6.1 through 6.3 for a cyclic input with different rest periods between cycles. It is precisely this type of behavior that is characteristic of the rehealing phenomenon that plagues and complicates the behavior of many filled polymeric materials. It appears that by incorporating $||f||_{h,p}$ norms into the kernel functions of the constitutive equations proposed at the end of section 5, constitutive equations for materials with permanent memory, fading memory, rehealable memory or any combination of these could be obtained.

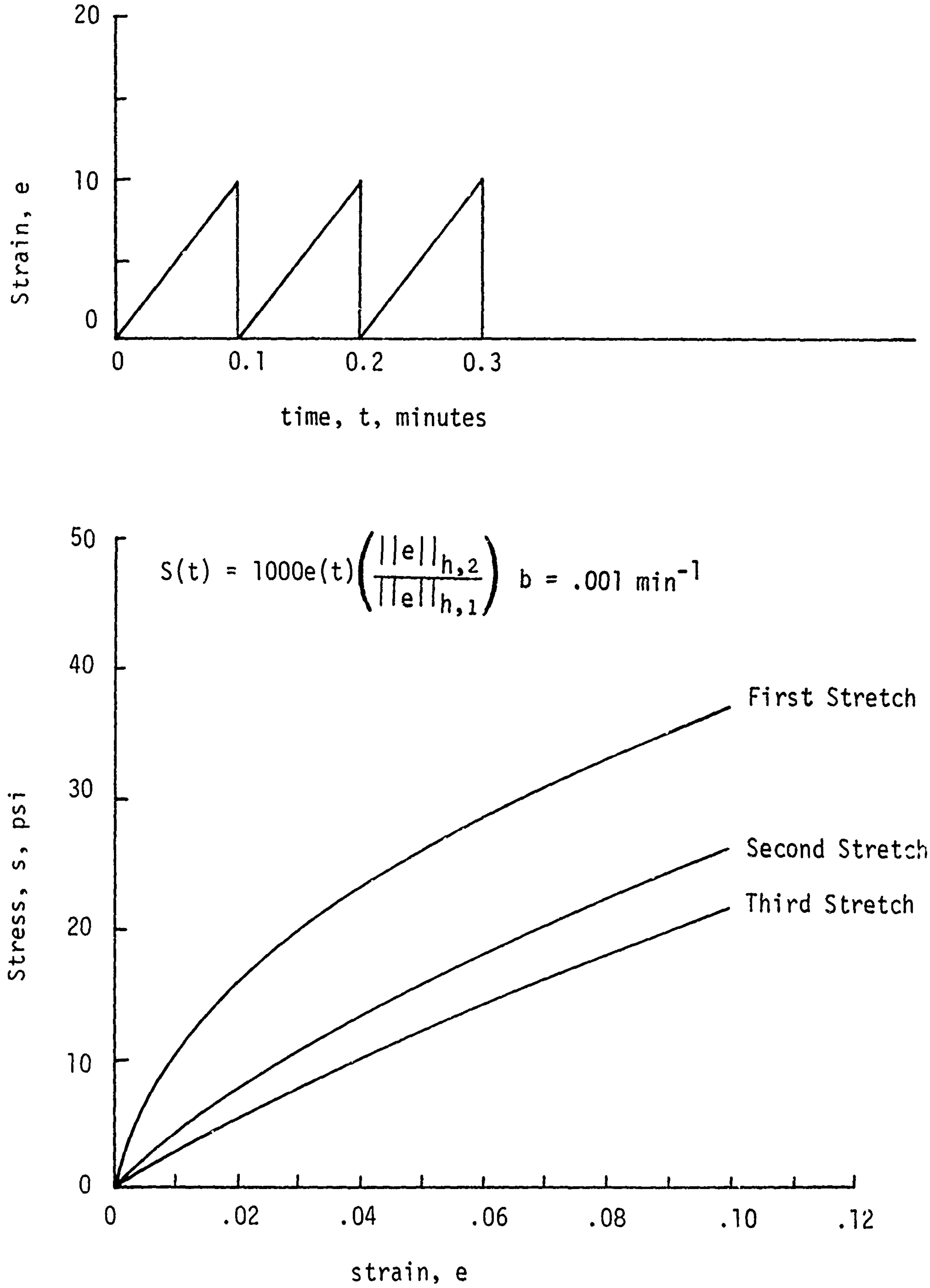
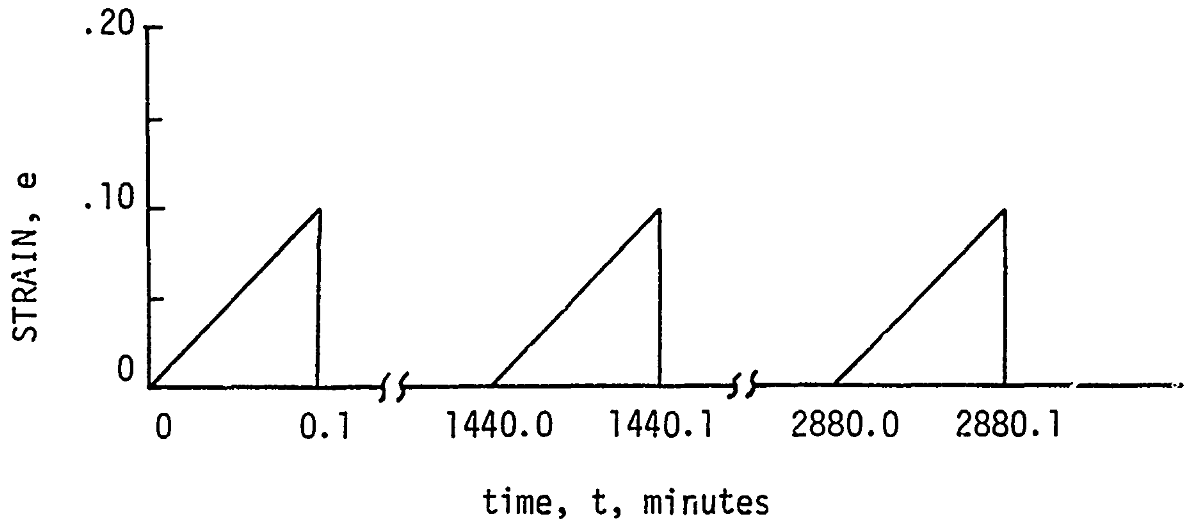


Figure 6.1. REPEATED RAMP TEST WITH NO REST PERIOD BETWEEN CYCLES.



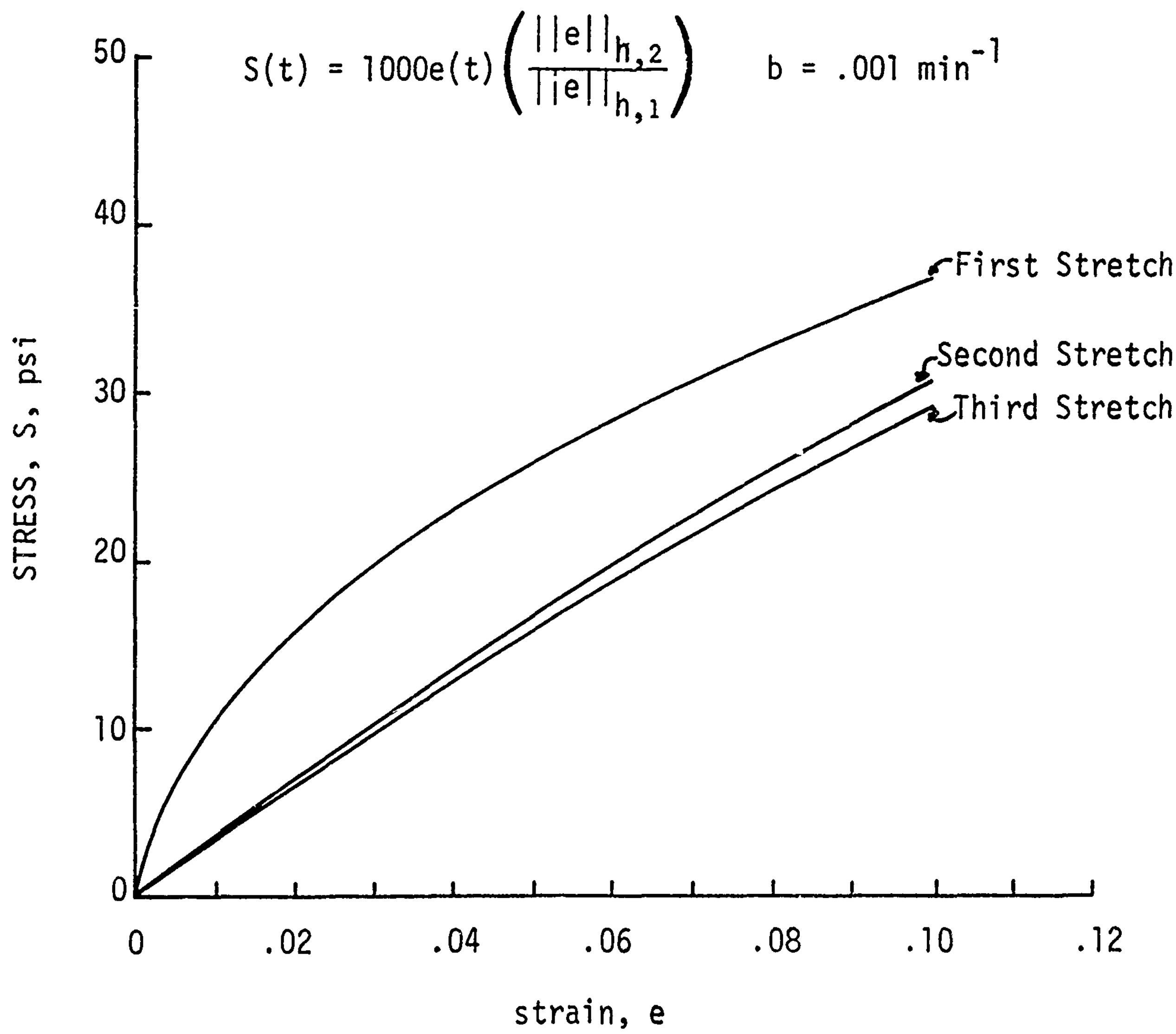
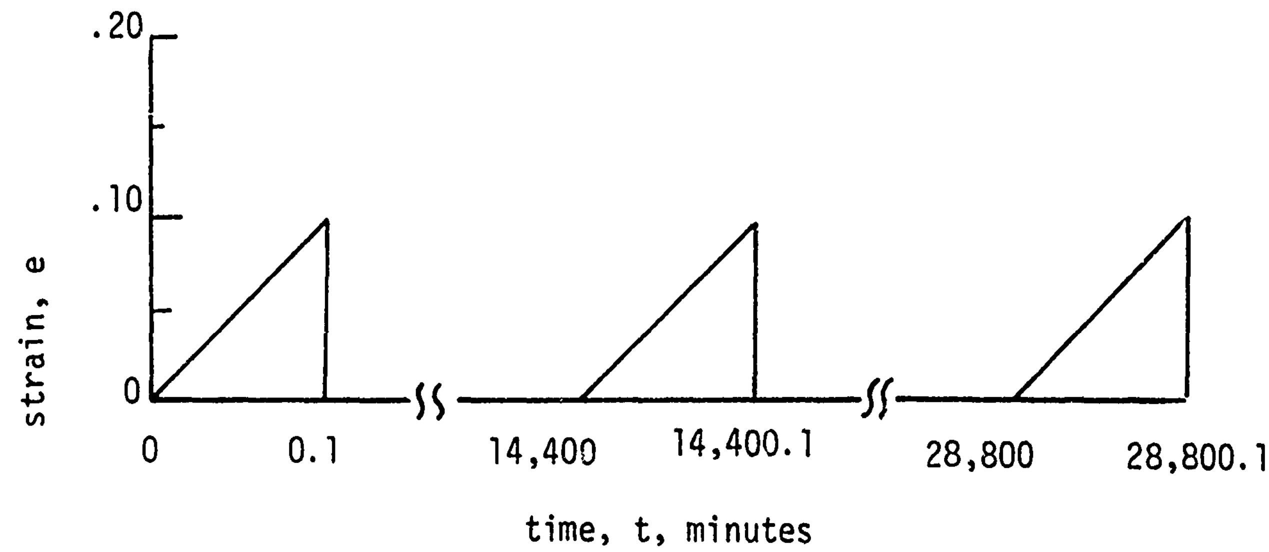


Figure 6.2. REPEATED RAMP TEST WITH 24 HOUR REST PERIOD BETWEEN CYCLES



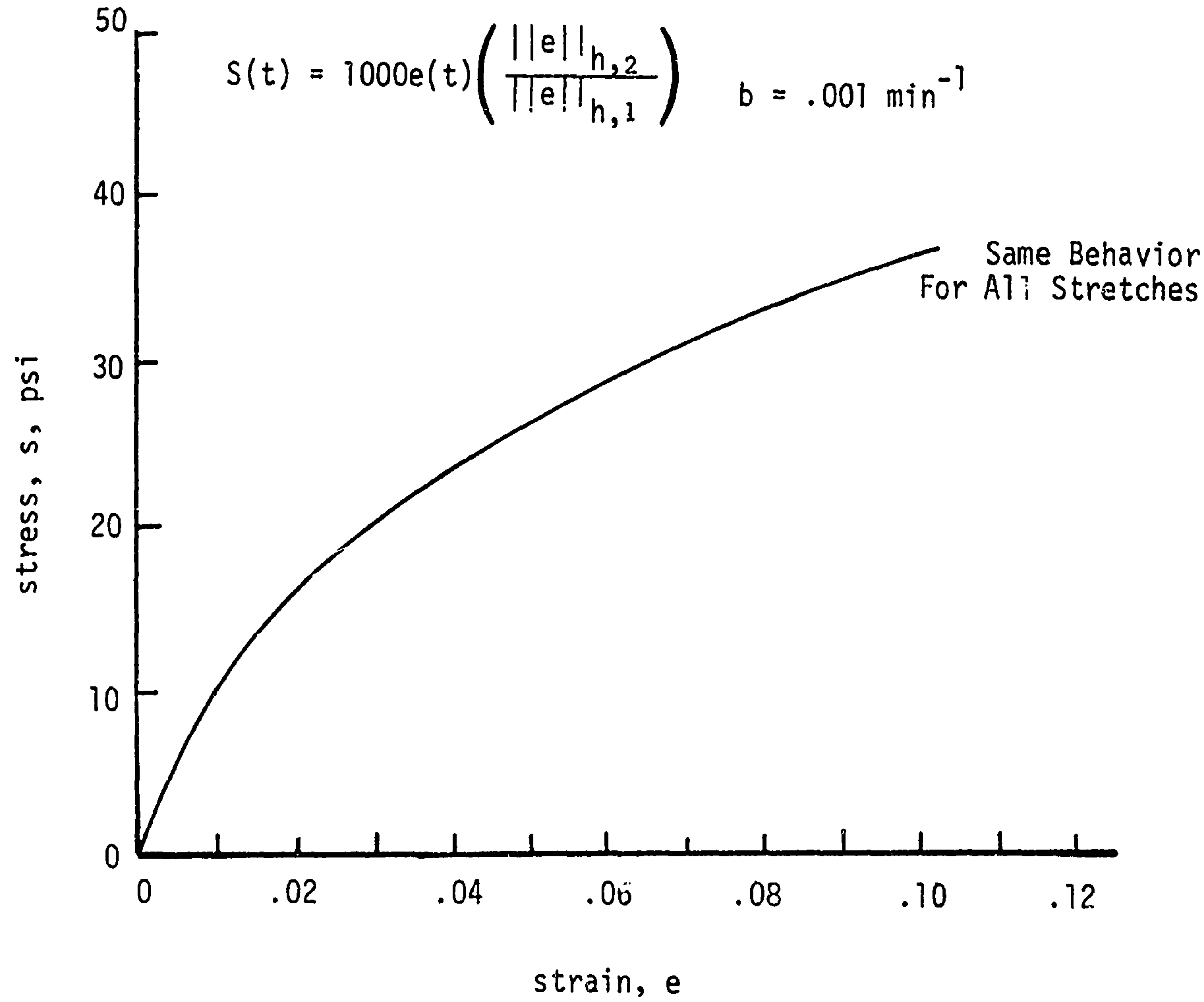


Figure 6.3. REPEATED RAMP TEST WITH 240 HOUR REST PERIOD BETWEEN CYCLES

These constitutive equations are not simply curve fitting exercises but can be used in three dimensional stress analysis in a simple, straight-forward manner as will be demonstrated in section 8.

VII. THERMORHEOLOGICALLY SIMPLE MATERIALS

In the previous sections homogeneous constitutive equations were developed for materials with a large class of memories. The equations were restricted to constant temperature conditions. It is well known that time effects such as relaxation, creep, and the rehealing phenomena are strongly temperature dependent [5,59]. If all the temperature effects are of the classical thermorheologically simple type [19,45,47,48,49] (where an equivalence between time and temperature exists), then a constitutive equation can be obtained that accounts for transient as well as constant temperature environments. The equivalence between time and temperature has been well documented by a number of researchers for polymeric materials [19,45,47], and others have given phenomenological as well as theoretical reasons for its existence. It can be shown for example in the spring-dashpot models of linear viscoelasticity that if the viscosity of the dashpots all have the same relative temperature dependence, and the spring constants are all independent of temperature, then time-temperature superposition and hence thermorheologically simple behavior is valid [47]. The assumption of thermorheologically simple materials is not restricted to the domain of linear materials. It is purely a mathematical relationship between a reduced time and the real time-temperature history at a point. The standard definition of reduced time which will be called t' and its generic value which will be called τ' or ξ' are

$$\xi'(\tau) = \tau'(\tau) = \int_0^\tau A[\theta(\xi)]d\xi, \text{ and} \qquad (7.1a)$$

$$t' = \tau'(t) = \int_0^t A[\theta(\xi)]d\xi \ , \tag{7.1b}$$

where $\theta(\xi)$ is the temperature-time history and A is a positive function. Providing the assumption of thermorheological simplicity is valid, the homogeneous constitutive equation of degree one would now become*

$$S_{ij}(t') = \delta_{ij}\int_0^{t'} K_0\left[I_1(\overset{t'}{\underset{0}{\xi'}}),I_2(\overset{t'}{\underset{0}{\xi'}}),I_3(\overset{t'}{\underset{0}{\xi'}}),t'-\tau'\right]\dot{e}_{kk}(\tau')d\tau'$$

$$+ \int_0^{t'} K_1\left[I_1(\overset{t'}{\underset{0}{\xi'}}),I_2(\overset{t'}{\underset{0}{\xi'}}),I_3(\overset{t'}{\underset{0}{\xi'}}),t'-\tau'\right]\dot{e}_{ij}(\tau')d\tau' ,$$

where

$$K_i\left[aI_1(\overset{t'}{\underset{0}{\xi'}}),a^2I_2(\overset{t'}{\underset{0}{\xi'}}),a^3I_3(\overset{t'}{\underset{0}{\xi'}}),t'-\tau'\right] =$$

$$K_i\left[I_1(\overset{t'}{\underset{0}{\xi'}}),I_2(\overset{t'}{\underset{0}{\xi'}}),I_3(\overset{t'}{\underset{0}{\xi'}}),t'-\tau'\right] \ . \tag{7.2}$$

Since the strain input is only a time function and

$$\frac{\partial e_{pq}}{\partial \tau'}d\tau' = \frac{\partial e_{pq}}{\partial \tau}d\tau = de_{pq} \ , \tag{7.3}$$

the equation can also be expressed as

$$S_{ij}(t) = \delta_{ij}\int_0^{t} K_0\left[I_1(\overset{t'}{\underset{0}{\xi'}}),I_2(\overset{t'}{\underset{0}{\xi'}}),I_3(\overset{t'}{\underset{0}{\xi'}}),t'-\tau'\right]\dot{e}_{kk}(\tau)d\tau$$

$$+ \int_0^{t} K_1\left[I_1(\overset{t'}{\underset{0}{\xi'}}),I_2(\overset{t'}{\underset{0}{\xi'}}),I_3(\overset{t'}{\underset{0}{\xi'}}),t'-\tau'\right]\dot{e}_{ij}(\tau)d\tau \ . \tag{7.4}$$

* Three reduced times were defined instead of the conventional two to eliminate confusion as to what variables enter into the integration process in equation (7.2).

Equation (7.4) is often times much simpler to use than equation (7.2) since $\dot{e}_{pq}(\tau)$ is controlled in some forms of experimental data.

Since propellant materials tested at constant temperature normally exhibit time-temperature superposition [15,18,45], it appears that this form of the constitutive equation could be an excellent approximation of their behavior. In equation (7.2) or (7.4) the form for the kernel functions has not been specified. If the kernel functions are to be represented as $||f||_p$ or $||f||_{h,p}$ norms, no complications arise as the reduced time t and its generic value ξ' or τ' simply replace the real time t and its generic value τ or ξ in the equations, whether they be norms, functionals or functions. The definition of the norm for a reduced time scale would be

$$||f||^r_{h,p} = \left\{\int_0^{t'} (|f(\xi')|h(t'-\xi'))^p d\xi'\right\}^{1/p} \quad , \qquad (7.5)$$

where the superscript r denotes the norm is with respect to reduced time.

From such a norm it is apparent that increasing the temperature could greatly change the rate of annihilation of memory.

To demonstrate the simplicity and effectiveness of the reduced time, consider again the one dimensional constitutive equation in terms of the $||f||^r_p$ norms.

$$S(t) = B\, e(t)\left[||e||^r_p \Big/ ||e||^r_q\right], \text{ where } p>q \quad . \qquad (7.6)$$

If the temperature is constant, the reduced time simply becomes

$$t' = A(\theta)t, \text{ and}$$

$$\xi' = A(\theta)\xi \quad . \tag{7.7}$$

For the case of stress-relaxation tests it is found that

$$||e_0||_p^r = |e_0| \, (A(\theta)t)^{1/p}, \text{ and}$$

$$||e_0||_q^r = |e_0| \, (A(\theta)t)^{1/q} \quad . \tag{7.8}$$

The stress-time output for this test simply becomes a power law in the reduced time.

$$S(t) = B\, e_0[A(\theta)t]^{\frac{1}{p} - \frac{1}{q}} = Ae_0 t'^{-n} \quad \text{, where } n = \frac{1}{q} - \frac{1}{p} \quad . \tag{7.9}$$

In fact, if the material is thermorheologically simple, the stress-real time output from two similar tests performed at different temperatures can be superposed on a s(t) vs Log t plot by simply shifting along the time axis. The amount of shift required is precisely log $[A(\theta_1)/A(\theta_2)]$, where θ_1 and θ_2 were the two test temperatures. This shift ability of stress-time data for equivalent tests will be true for linear or nonlinear materials, no matter how the stress functional is represented.

VIII. SOLUTION OF BOUNDARY VALUED PROBLEMS

The equations developed thus far are non-linear but homogeneous constitutive equations of degree one that describe a large class of memory phenomena. For the special case of thermorheologically simple materials the equations have been expressed in terms of reduced time variables thereby encompassing an even larger class of behaviors. The purpose of this section is to demonstrate the applicability of this type of constitutive equation in the solution of either stress or displacement boundary valued problems. The types of problems considered will be proportional boundary valued problems with constant body forces and no inertial effects. By a proportional boundary valued problem it is meant that the conditions at the boundary surface are given as a single product term involving a spatial function and a time function. Since no inertial effects are being accounted for, the time variance of the boundary conditions must be reasonably slow or quasi-static to justify having no inertia terms in the equations of equilibrium. Proportional boundary value problems encompass a majority of the engineering problems encountered since they can allow for the boundary values to change with time. For linear elasticity or linear viscoelasticity, the procedure for developing a solution is straightforward since all the equations that must be solved are linear and superposition is applicable. For non-linear materials however, one is quite fortunate if a large class of problems can be contained in a solution scheme. Such is the case for the homogeneous constitutive equation of degree one.

8.1 Proportional Stress Boundary Valued Problems

In the introduction of this section it was indicated that the solution to proportional boundary valued problems could be obtained for non-linear constitutive equations homogeneous to degree one. For plane strain or plane stress problems which have proportional stress boundary values it is found that a linear elastic solution for the stresses is a solution for the stress-time distribution whenever the kernel functionals of the constitutive equation can be decomposed into a product form. The strain-time distribution for this case will be given by substituting the linear stress solution into the non-linear constitutive equation which is homogeneous to degree one. That such a solution is applicable is demonstrated in the following discussion.

By a proportional stress boundary valued problem it is meant that the boundary conditions are space and time separable.

$$S_{ij}(x_k,\tau)\nu_j(x_k) = \overset{\circ}{S}_{ij}(x_k)\nu_j(x_k)f(\tau), \quad \text{all } x_k \varepsilon \text{ boundary.}$$

where ν_j = direction cosines of a unit vector normal to the boundary

$\overset{\circ}{s}_{ij}(x_k)$ = stresses prescribed at some reference time

$f(\tau)$ = time function (8.1)

In the above description it was assumed that the boundary position does not change significantly with time which naturally restricts this discussion to infinitesimal strain theory. Hence the strain tensor

in the constitutive equation will be given as the Cauchy strain tensor e_{ij} where

$$e_{ij} = \frac{1}{2}\,(\partial u_i/\partial x_j + \partial u_j/\partial x_i). \tag{8.2}$$

With this definition of strain, the constitutive equation becomes

$$\begin{aligned} e_{ij}(x_k,t) = \delta_{ij} \int_0^t L_0\Big[J_1(x_k,\overset{t}{\underset{o}{\xi}}),J_2(x_k,\overset{t}{\underset{o}{\xi}}),J_3(x_k,\overset{t}{\underset{o}{\xi}}),t-\tau\Big]\dot{S}_{ii}(x_k,\tau)d\tau \\ + \int_0^t L_1\Big[J_1(x_k,\overset{t}{\underset{o}{\xi}}),J_2(x_k,\overset{t}{\underset{o}{\xi}}),J_3(x_k,\overset{t}{\underset{o}{\xi}}),t-\tau\Big]\dot{S}_{ij}(x_k,\tau)d\tau. \end{aligned} \tag{8.3}$$

The kernel functionals in equation (8.3) were specified as being homogeneous to degree zero. Note that the kernel functionals contain spatial measures since the invariants are simply combinations of the stress which except in trivial cases, are functions of the spatial coordinates x_k. For the purpose of clarity, assume that a linear elastic solution for the stresses within the body is valid. For the proportional boundary valued problem this linear elastic solution can be represented as

$$S_{ij}(x_k,\tau) = \overset{o}{S}_{ij}(x_k)f(\tau)\ ,$$

$$\text{all } x_k \varepsilon \text{ volume, and } 0 \le \tau \le t\ . \tag{8.4}$$

8.1 Proportional Stress Boundary Valued Problems

In the introduction of this section it was indicated that the solution to proportional boundary valued problems could be obtained for non-linear constitutive equations homogeneous to degree one. For plane strain or plane stress problems which have proportional stress boundary values it is found that a linear elastic solution for the stresses is a solution for the stress-time distribution whenever the kernel functionals of the constitutive equation can be decomposed into a product form. The strain-time distribution for this case will be given by substituting the linear stress solution into the non-linear constitutive equation which is homogeneous to degree one. That such a solution is applicable is demonstrated in the following discussion.

By a proportional stress boundary valued problem it is meant that the boundary conditions are space and time separable.

$$S_{ij}(x_k,\tau)\nu_j(x_k) = S^{\circ}_{ij}(x_k)\nu_j(x_k)f(\tau), \quad \text{all } x_k \varepsilon \text{ boundary.}$$

where ν_j = direction cosines of a unit vector normal to the boundary

$s^{\circ}_{ij}(x_k)$ = stresses prescribed at some reference time

$f(\tau)$ = time function (8.1)

In the above description it was assumed that the boundary position does not change significantly with time which naturally restricts this discussion to infinitesimal strain theory. Hence the strain tensor

in the constitutive equation will be given as the Cauchy strain tensor e_{ij} where

$$e_{ij} = \frac{1}{2} (\partial u_i/\partial x_j + \partial u_j/\partial x_i). \tag{8.2}$$

With this definition of strain, the constitutive equation becomes

$$e_{ij}(x_k,t) = \delta_{ij} \int_0^t L_0\left[J_1(x_k,\underset{0}{\overset{t}{\xi}}),J_2(x_k,\underset{0}{\overset{t}{\xi}}),J_3(x_k,\underset{0}{\overset{t}{\xi}}),t-\tau\right]\dot{S}_{ii}(x_k,\tau)d\tau$$
$$+ \int_0^t L_1\left[J_1(x_k,\underset{0}{\overset{t}{\xi}}),J_2(x_k,\underset{0}{\overset{t}{\xi}}),J_3(x_k,\underset{0}{\overset{t}{\xi}}),t-\tau\right]\dot{S}_{ij}(x_k,\tau)d\tau. \tag{8.3}$$

The kernel functionals in equation (8.3) were specified as being homogeneous to degree zero. Note that the kernel functionals contain spatial measures since the invariants are simply combinations of the stress which except in trivial cases, are functions of the spatial coordinates x_k. For the purpose of clarity, assume that a linear elastic solution for the stresses within the body is valid. For the proportional boundary valued problem this linear elastic solution can be represented as

$$S_{ij}(x_k,\tau) = \overset{\circ}{S}_{ij}(x_k)f(\tau) ,$$
$$\text{all } x_k \varepsilon \text{ volume, and } 0 \leq \tau \leq t . \tag{8.4}$$

In equation (8.4) $\overset{\circ}{S}_{ij}(x_k)$ is the solution to the boundary valued problem when $f(\tau)= 1$. This proportionality of the solution is a direct consequence of the first linearity rule. If the linear elastic solution for the stresses is valid, then the stress invariants $J_i(x_k,\xi)$ are given as

$$J_1(x_k,\xi) = J_1^\circ(x_k)f(\xi),$$
$$J_2(x_k,\xi) = J_2^\circ(x_k)f^2(\xi), \text{ and}$$
$$J_3(x_k,\xi) = J_3^\circ(x_k)f^3(\xi), \quad \text{for all } x_k \varepsilon \text{ volume and } 0 \leq \xi \leq t. \tag{8.5}$$

In equation (8.5) the invariants $J_i^\circ(x_k)$ are simply the values of the invariants when the time function $f(\xi)$ is equal to unity. Observe that at some particular location within the body $x_k=(a_1,a_2,a_3)$ the invariants are given as

$$J_i(x_k,\xi) = J_i^\circ(a_1,a_2,a_3)f^i(\xi),$$
$$\text{where } \overset{\circ}{J}_i(a_1,a_2,a_3) = \text{constant function.} \tag{8.6}$$

Assuming now that the kernel functions can be separated into product functions yields

$$L_i\left[J_1(x_k,\overset{t}{\underset{0}{\xi}}),J_2(x_k,\overset{t}{\underset{0}{\xi}}),J_3(x_k,\overset{t}{\underset{0}{\xi}}),t-\tau\right] =$$
$$= \sum_{r=1}^{N} M_{ir}\left[J_1(x_k,\overset{t}{\underset{0}{\xi}}),t-\tau\right]N_{ir}\left[J_2(x_k,\overset{t}{\underset{0}{\xi}}),t-\tau\right]P_{ir}\left[J_3(x_k,\overset{t}{\underset{0}{\xi}}),t-\tau\right]. \tag{8.7}$$

Recall that these kernel functions L_0 and L_1 were homogeneous to degree zero which means

$$L_i\left[aJ_1(x_k,\overset{t}{\underset{0}{\xi}}),a^2J_2(x_k,\overset{t}{\underset{0}{\xi}}),a^3J_3(x_k,\overset{t}{\underset{0}{\xi}}),t-\tau\right] =$$

$$L_i\left[J_1(x_k,\overset{t}{\underset{0}{\xi}}),J_2(x_k,\overset{t}{\underset{0}{\xi}}),J_3(x_k,\overset{t}{\underset{0}{\xi}}),t-\tau\right] ,$$

where a is an arbitrary constant and $s_{pq}(\tau)$ are arbitrary. (8.8)

Therefore, it is required that each of the components of the kernel decomposition be likewise homogeneous to degree zero. Substituting the invariants given by equation (8.6) into equation (8.7) produces

$$M_{ir}\left[J_1(x_k,\overset{t}{\underset{0}{\xi}}),t-\tau\right] = M_{ir}\left[\overset{\circ}{J}_1(x_k)f(\overset{t}{\underset{0}{\xi}}),t-\tau\right],$$

$$N_{ir}\left[J_2(x_k,\overset{t}{\underset{0}{\xi}}),t-\tau\right] = N_{ir}\left[\overset{\circ}{J}_2(x_k)f^2(\overset{t}{\underset{0}{\xi}}),t-\tau\right], \text{ and}$$

$$P_{ir}\left[J_3(x_k,\overset{t}{\underset{0}{\xi}}),t-\tau\right] = P_{ir}\left[\overset{\circ}{J}_3(x_k)f^3(\overset{t}{\underset{0}{\xi}}),t-\tau\right] . \qquad (8.9)$$

The constitutive equation gives the strain at some arbitrary, but fixed, point within the body. At some fixed point in space, however, the functions $\overset{\circ}{J}_1(x_k)$, $\overset{\circ}{J}_2(x_k)$, and $\overset{\circ}{J}_3(x_k)$ are simply constants. Since the kernel functions M_{ir}, P_{ir}, and N_{ir} were specified as being homogeneous to degree zero, these constants

have no effect on the values these kernels take on. For the special case when a linear elastic solution is valid and the kernels can be decomposed, the conclusion is as follows

$$M_{ir}\left[J_1(x_k,\overset{t}{\underset{0}{\xi}}),t-\tau\right] = M_{ir}\left[\overset{\circ}{J}_1(x_k)f(\overset{t}{\underset{0}{\xi}}),t-\tau\right] = M_{ir}\left[f(\overset{t}{\underset{0}{\xi}}),t-\tau\right] ,$$

$$N_{ir}\left[J_2(x_k,\overset{t}{\underset{0}{\xi}}),t-\tau\right] = N_{ir}\left[\overset{\circ}{J}_2(x_k)f^2(\overset{t}{\underset{0}{\xi}}),t-\tau\right] = N_{ir}\left[f^2(\overset{t}{\underset{0}{\xi}}),t-\tau\right],$$

$$P_{ir}\left[J_3(x_k,\overset{t}{\underset{0}{\xi}}),t-\tau\right] = P_{ir}\left[\overset{\circ}{J}_3(x_k)f^3(\overset{t}{\underset{0}{\xi}}),t-\tau\right] = P_{ir}\left[f^3(\overset{t}{\underset{0}{\xi}}),t-\tau\right]. \quad (8.10)$$

Note that the kernel functions now contain no spatial variables and are only functions of the history of $f(\xi)$ and the variable $t-\tau$. Since the forms of these kernels are still arbitrary, there is no loss in generality by assuming that a functional of $f^2(\xi)$ or $f^3(\xi)$ is contained in a general functional of $f(\xi)$. Therefore the assumptions of a linear elastic solution for the stresses and separable kernels results in

$$L_i\left[J_1(x_k,\overset{t}{\underset{0}{\xi}}),J_2(x_k,\overset{t}{\underset{0}{\xi}}),J_3(x_k,\overset{t}{\underset{0}{\xi}}),t-\tau\right] =$$

$$= L_i\left[f(\overset{t}{\underset{0}{\xi}}),f^2(\overset{t}{\underset{0}{\xi}}),f^3(\overset{t}{\underset{0}{\xi}}),t-\tau\right] = L_i'\left[f(\overset{t}{\underset{0}{\xi}}),t-\tau\right] . \quad (8.11)$$

Dropping the prime notation in the last of equation (8.11) the constitutive equation now becomes

$$e_{ij}(x_k,t) = \delta_{ij}\int_0^t L_1\left[f(\overset{t}{\underset{0}{\xi}}),t-\tau\right]\dot{S}_{ii}(x_k,\tau)d\tau +$$

$$+\int_0^t L_2\left[f(\overset{t}{\underset{0}{\xi}}),t-\tau\right]\dot{S}_{ij}(x_k,\tau)d\tau . \quad (8.12)$$

Equation (8.12) would be identical to the linear viscoelastic constitutive equation if the kernels L_0 and L_1 were independent of $f(\xi)$. Because $f(\xi)$ is present in the equation, linear transforms cannot be utilized on the constitutive equation to demonstrate that the assumed linear elastic solution for the stresses is valid. If it can be shown that equation (8.12) will satisfy the equations of equilibrium and compatibility whenever the linear elastic solution is valid, a type of correspondence principle will have been developed similar to what has already been done in the theory of linear viscoelasticity. The validity of the elastic solution can be demonstrated by substituting the constitutive equation directly into the equations of equilibrium and compatibility. It should be immediately obvious that no complications can arise in such a procedure since the only spatially dependent quantities in the constitutive equation are the stresses s_{ij} and the strains e_{ij}. For the two dimensional problem only one equation of compatibility* is present,

$$\frac{\partial^2 e_{11}(x_k,t)}{\partial x_2{}^2} + \frac{\partial^2 e_{22}(x_k,t)}{\partial x_1{}^2} = \frac{2\partial^2 e_{12}(x_k,t)}{\partial x_1 \partial x_2} \qquad (8.13)$$

Substituting the constitutive equation directly into the compatibility equation and interchanging the roles of integration

*There are other compatibility conditions for plane stress that are sometimes not satisfied by this method. See Timoshenko and Goodier [22], page 25.

and differentiation equation (8.13) becomes

$$\int_0^t \left\{ L_0\left[\overset{t}{\underset{o}{f(\xi)}},t-\tau\right]\nabla^2\dot{S}_{ii}(x_k,\tau) + L_1\left[\overset{t}{\underset{o}{f(\xi)}},t-\tau\right]\left(\frac{\partial^2\dot{S}_{11}(x_k,\tau)}{\partial x_2{}^2} + \frac{\partial^2\dot{S}_{22}(x_k,\tau)}{\partial x_1{}^2}\right)\right.$$

$$\left. - 2L_1\left[\overset{t}{\underset{o}{f(\xi)}},t-\tau\right] \frac{\partial^2\dot{S}_{12}(x_k,\tau)}{\partial x_1\partial x_2} \right\} d\tau = 0 \quad . \qquad (8.14)$$

The equilibrium equations for a two dimensional problem are

$$\frac{\partial S_{11}(x_k,\tau)}{\partial x_1} + \frac{\partial S_{12}(x_k,\tau)}{\partial x_2} + \overline{X}_1 = 0 \ , \quad \text{and}$$

$$\frac{\partial S_{12}(x_k,\tau)}{\partial x_1} + \frac{\partial S_{22}(x_k,\tau)}{\partial x_2} + \overline{X}_2 = 0 \ , \qquad (8.15)$$

where $\overline{X}_i$ are body forces and were specified as being constant.

Differentiating the first equilibrium equation with respect to x_1, the second with respect to x_2 and adding the following is obtained

$$2\,\frac{\partial^2 S_{12}(x_k,\tau)}{\partial x_1\partial x_2} = -\left(\frac{\partial^2 S_{11}(x_k,\tau)}{\partial x_1{}^2} + \frac{\partial^2 S_{22}(x_k,\tau)}{\partial x_2{}^2}\right) \qquad (8.16)$$

Substituting this result into equation (8.14) yields

$$\int_0^t \left\{ L_0\left[\overset{t}{\underset{0}{f(\xi)}},t-\tau\right]\nabla^2\dot{S}_{ii}(x_k,\tau) + L_1\left[\overset{t}{\underset{0}{f(\xi)}},t-\tau\right]\nabla^2\left[\dot{S}_{11}(x_k,\tau) + \dot{S}_{22}(x_k,\tau)\right]\right\} d\tau = 0,$$

where $\nabla^2 = \frac{\partial^2}{\partial x_1{}^2} + \frac{\partial^2}{\partial x_2{}^2}$. (8.17)

8.2 Specialization to Plane Stress

For the condition of plane stress $s_{33}(x_k,\tau) = 0$, with this restriction equation (8.17) reduces to

$$\int_0^t \left\{ \left(L_0\left[\overset{t}{\underset{0}{f(\xi)}},t-\tau\right] + L_1\left[\overset{t}{\underset{0}{f(\xi)}},t-\tau\right]\right)\frac{\partial}{\partial\tau}\nabla^2 S_{ii}(x_k,\tau)\right\} d\tau = 0 . \qquad (8.18)$$

A sufficient condition to make the integral in equation (8.18) vanish is to require that

$$\nabla^2 \overset{\circ}{S}_{ii}(x_k) = 0 \ , \quad \text{since } S_{ii}(x_k,\tau) = f(\tau)\overset{\circ}{S}_{ii}(x_k) \qquad (8.19)$$

Equation (8.19) is precisely the identical condition placed on the stress distribution for a linear elastic body. The assumption made in equation (8.4) therefore in no way violates the equations of equilibrium or compatibility.

8.3 Specialization to Plane Strain

For the condition of plane strain $e_{33}(x_k,t) = 0$, therefore taking the Laplacian of the constitutive equation produces

$$0 = \nabla^2 e_{33}(x_k,t) = \int_0^t \left\{ L_0\left[\overset{t}{\underset{0}{f(\xi)}},t-\tau\right]\nabla^2\dot{S}_{ii}(x_k,\tau) + L_1\left[\overset{t}{\underset{0}{f(\xi)}},t-\tau\right]\nabla^2\dot{S}_{33}(x_k\tau)\right\} d\tau.$$

(8.20)

Substituting this restriction into 8.17) gives

$$\int_0^t L_1\left[\overset{t}{\underset{0}{f(\xi)}},t-\tau\right]\frac{\partial}{\partial\tau}\nabla^2 S_{ii}(x_k,\tau)d\tau = 0 \ . \qquad (8.21)$$

In order to require this integral to vanish for all times and all space a sufficient condition is to require

$$\nabla^2 \overset{\circ}{S}_{ii}(x_k) = 0, \quad \text{since } S_{ii}(x_k,\tau) = f(\tau)\overset{\circ}{S}_{ii}(x_k) \qquad (8.22)$$

Equation (8.22) is again the exact condition placed on a plane strain solution for a linear elastic solid.

For the case of plane strain and plane stress a type of correspondence principle between the linear elastic solution and the solution for a homogeneous but non-linear material has been established. This correspondence principle can be stated as follows:

CORRESPONDENCE PRINCIPLE 1.

Given a plane strain or plane stress proportional boundary valued problem of the form

i) $S_{ij}(x_k,\tau)\nu_j(x_k) = \overset{\circ}{S}_{ij}(x_k)\nu_j(x_k)f(\tau) \quad x_k \varepsilon$ Boundary and $0 \leq \tau \leq t$

for a material having a non-linear but homogeneous constitutive equation of degree one of the form

$$ii) \quad e_{ij}(x_k,t) = \delta_{ij}\int_0^t L_0\left[J_1(x_k,\overset{t}{\underset{0}{\xi}}),J_2(x_k,\overset{t}{\underset{0}{\xi}}),J_3(x_k,\overset{t}{\underset{0}{\xi}}),t-\tau\right]\dot{S}_{ii}(x_k,\tau)d\tau$$
$$+\int_0^t L_1\left[J_1(x_k,\overset{t}{\underset{0}{\xi}}),J_2(x_k,\overset{t}{\underset{0}{\xi}}),J_3(x_k,\overset{t}{\underset{0}{\xi}}),t-\tau\right]\dot{S}_{ij}(x_k,\tau)d\tau \ .$$

Then a plane strain or plane stress linear elastic solution for the stress distribution is valid and when substituted into the non-linear constitutive equation, the equations of equilibrium and compatibility used in two dimensional elasticity will be identically satisfied provided

1) *the body forces are constant*

2) *the kernel functions can be decomposed into a product form, each term of which only involves one invariant history* $J_i(x_k, \overset{t}{\underset{0}{\xi}})$ *and the variable* $t-\tau$.

The strains can then be obtained by substituting the time dependent elastic solution into the non-linear constitutive equation which can be reduced to the form

$$iii)\quad e_{ij}(x_k,t) = \delta_{ij} \overset{\circ}{S}_{ii}(x_k) \int_0^t L_0\left[f(\overset{t}{\underset{0}{\xi}}), t-\tau\right] \dot{f}(\tau)d\tau + \overset{\circ}{S}_{ij}(x_k) \int_0^t L_1\left[f(\overset{t}{\underset{0}{\xi}}), t-\tau\right] \dot{f}(\tau)d\tau.$$

8.4 Correspondence Principles for Three Dimensional Problems

Other correspondence principles can be developed by the same method by first assuming a solution of a particular form exists and then showing what conditions are necessary to satisfy the equilibrium and compatibility equations. In this manner the following correspondence principles can be developed.

CORRESPONDENCE PRINCIPLE 2.

Given a three dimensional proportional boundary valued problem of the form

i) $S_{ij}(x_k,\tau)\nu_j(x_k) = S^{\circ}_{ij}(x_k)\nu_j(x_k)f(\tau) \quad x_k \varepsilon$ Boundary, and $0 \leq \tau \leq t$

for a material having a non-linear but homogeneous constitutive equation of degree one of the form

$$ii)\quad e_{ij}(x_k,\tau) = \delta_{ij}\int_0^t L_0\left[J_1(x_k,\overset{t}{\underset{0}{\xi}}),J_2(x_k,\overset{t}{\underset{0}{\xi}}),J_3(x_k,\overset{t}{\underset{0}{\xi}}),t-\tau\right]\dot{S}_{ii}(x_k,\xi)d\tau$$

$$+\int_0^t L_1\left[\dot{J}_1(x_k,\overset{t}{\underset{0}{\xi}}),J_2(x_k,\overset{t}{\underset{0}{\xi}}),J_2(x_k,\overset{t}{\underset{0}{\xi}}),t-\tau\right]\dot{S}_{ij}(x_k,\tau)d\tau \;.$$

Then a linear elastic solution for the stress distribution is valid and when substituted into the non-linear constitutive equation will satisfy identically the equations of equilibrium and compatibility provided

1) *the body forces are constant*
2) *the kernel functions can be decomposed into a product form, each term of which involves only one invariant history* $J_i(x_k,\overset{t}{\underset{0}{\xi}})$ *and the variable* $t-\tau$.
3) *the two kernel functionals* L_o *and* L_1 *are proportional to each other, the proportionality factor being a type of Poisson's ratio.* $L_1 = -\left[\frac{1+\mu}{\mu}\right]L_0$

The strains can then be calculated by substituting the time dependent elastic solution into the non-linear constitutive equation which can be reduced to the form

$$iii)\quad e_{ij}(x_k,t) = \left(\delta_{ij}\overset{\circ}{S}_{ii}(x_k) - \left(\frac{1+\mu}{\mu}\right)\overset{\circ}{S}_{ij}(x_k)\right)\int_0^t L_0\left[f\left(\overset{t}{\underset{0}{\xi}}\right),t-\tau\right]\dot{f}(\tau)d\tau \ ,$$

where μ *is Poisson's ratio.*

CORRESPONDENCE PRINCIPLE 3.

Given a three dimensional proportional displacement boundary valued problem of the form

$$i)\quad u_i(x_k,\tau) = \overset{\circ}{u}_i(x_k)f(\tau)\ , \qquad x_k \varepsilon \text{ Boundary},\ 0 \le \tau \le t$$

for a material having a non-linear but homogeneous constitutive equation of degree one of the form

$$ii)\quad S_{ij}(x_k,t) = \delta_{ij}\int_0^t K_0\left[I_1\left(x_k,\overset{t}{\underset{0}{\xi}}\right),I_2\left(x_k,\overset{t}{\underset{0}{\xi}}\right),I_3\left(x_k,\overset{t}{\underset{0}{\xi}}\right),t-\tau\right]\dot{e}_{ii}(x_k,\tau)d\tau$$

$$+\int_0^t K_1\left[I_1\left(x_k,\overset{t}{\underset{0}{\xi}}\right),I_2\left(x_k,\overset{t}{\underset{0}{\xi}}\right),I_3\left(x_k,\overset{t}{\underset{0}{\xi}}\right),t-\tau\right]\dot{e}_{ij}(x_k,\tau)d\tau\ .$$

Then a linear elastic solution for the displacements or strains is valid and will satisfy the equations of equilibrium and compatibility when substituted into the non-linear constitutive equation provided

1) *there are no body forces*

2) *the two kernel functionals* K_o *and* K_1 *can be decomposed into a product form, each term of which involves only one-invariant history* $I_i[x_k, \overset{t}{\underset{0}{\xi}}]$ *and the variable* $t-\tau$.

3) *the two kernel functionals* K_o *and* K_1 *are portional to each other, the proportionality factor being a type of Poisson's ratio.*

$K_1 = (1-2\mu)\ K_0$

The stresses can then be calculated by substituting the elastic strain solution into the non-linear constitutive equation which can be reduced to

$$iii)\quad S_{ij}(x_k,t) = \left\{ e^{\circ}_{ii}(x_k)\delta_{ij} + (1-2\mu)e^{\circ}_{ij}(x_k) \right\} \int_0^t K_0\left[f(\overset{t}{\underset{0}{\xi}}), t-\tau \right] \dot{f}(\tau)d\tau.$$

CORRESPONDENCE PRINCIPLE 4.

Given a three-dimensional proportional boundary valued problem of the form

$$i)\quad S_{ij}(x_k,t)\nu_j(x_k) = S^{\circ}_{ij}(x_k)\nu_j(x_k)f(\tau) \qquad x_k \varepsilon \text{ Boundary},\ 0 \leq \tau \leq t$$

for a material possessing a non-linear but homogeneous constitutive equation of degree one of the form

$$ii)\quad e_{ij}(x_k,t) = G\left[f(\overset{t}{\underset{0}{\xi}}) \right] \left\{ \delta_{ij} \int_0^t L_0(t-\tau)\dot{S}_{ii}(x_k,\tau)d\tau + \int_0^t L_1(t-\tau)\dot{S}_{ij}(x_k,\tau)d\tau \right\}$$

Then a linear viscoelastic solution for the stress distribution is valid and when substituted into the non-linear constitutive equation, it will satisfy the equations of equilibrium and compatibility. The strains can then be calculated by substituting the stress history into the above constitutive equation.

CORRESPONDENCE PRINCIPLE 5.

Given a three-dimensional proportional boundary valued problem of the form

$$i)\quad u_i(x_k,\tau) = \overset{\circ}{u}_i(x_k)f(\tau) \qquad x_k \varepsilon \text{ Boundary},\ 0 \le \tau \le t$$

for a material having a non-linear but homogeneous constitutive equation of degree one of the form

$$ii)\quad S_{ij}(x_k,t) = H\left[\overset{t}{\underset{0}{f(\xi)}}\right]\left\{\delta_{ij}\int_0^t K_0(t-\tau)\dot{e}_{ii}(x_k,\tau)d\tau + \int_0^t K_1(t-\tau)\dot{e}_{ij}(x_k,\tau)d\tau\right\}$$

Then a linear viscoelastic solution for the strain distribution is valid and when substituted into the non-linear constitutive equation satisfies all the equations of equilibrium and compatibility. The stresses can then be calculated by substituting the strain history into the above constitutive equation.

It has been shown that every linear elastic or linearly visco-elastic solution to a proportional boundary valued problem corresponds also to half of the solution (either the stresses or the strains, but not both) to a similar problem for materials having homogeneous but

non-linear constitutive equations provided certain restrictions on the kernel functionals are imposed. For two dimensional stress boundary valued problems no additional restrictions were imposed. When the kernel functionals cannot be put into these forms, then it appears that no exact correspondence between the linear and non-linear solutions exist and other means of solution must be used. It should be pointed out however that most complex problems are solved using large computers whether the material be linear or non-linear. Numerical methods for the homogeneous constitutive equations should be fairly simple to develop or adapt to those already used for linear visco-elastic analysis no matter what the form of the kernel functionals. Hence structural analysis for this class of materials should be a straightforward extension of what has already been accomplished for linear materials. Since these correspondence principles do exist between the non-linear and linear solutions for materials having non-linear but homogeneous constitutive equations of degree one, they must be the simplest form of non-linear constitutive laws that are amendable to analytical methods.

8.5 Strain Induced Anisotropy

Often in the field of mechanics we hear the term "strain induced anisotropy." This type of behavior is not included in the constitutive equations proposed thus far in this thesis as the permanent memory phenomenon is recorded in the scalar invariant histories which are naturally the same for all directions. In order to include strain

induced anisotropy into the constitutive equations and still retain them homogeneous to degree one, the permanent memory measure must be some non-scalar quantity. Note that writing the usual isotropic constitutive equation with the kernel functionals being dependent on the history of $\overset{t}{\underset{o}{e_{pq}(\xi)}}$, or $\overset{t}{\underset{o}{s_{pq}(\xi)}}$, then the equations could contain strain or stress induced anisotropic behavior. However a homogeneous constitutive equation of degree one that includes strain or stress induced anisotropy for general non-proportional loading conditions can be shown to reduce to the isotropic constitutive equation if a linear solution is to be valid for a proportional problem.

For proportional problems, these kernel functions become

$$K_i\left[\overset{t}{\underset{o}{e_{pq}(x_k,\xi)}},t-\tau\right] = K_i\left[\overset{t}{\underset{o}{f(\xi)}},t-\tau\right] \quad \text{, or}$$

$$L_i\left[\overset{t}{\underset{o}{S_{pq}(x_k,\xi)}},t-\tau\right] = L_i\left[\overset{t}{\underset{o}{f(\xi)}},t-\tau\right]. \tag{8.23}$$

Note that for proportional boundary value problems a strain or stress-induced anisotropic constitutive equation will admit the same elastic solution as the purely isotropic equation. Furthermore, the strain or stress induced anisotropy has no influence on the solution and one could not use such a test to determine if the material had become anisotropic due to the loading. For non-proportional boundary value problems this type of anisotropy can greatly influence the analysis.

8.6 Uniqueness of Solution

Various methods of proving uniqueness of solution for the non-linear constitutive equations homogeneous to degree one have been attempted, but all have failed to demonstrate uniqueness of solution. Since the boundary conditions and the equations of equilibrium and compatibility are all linear, one can proceed in the usual manner [22-24] by first assuming two solutions s'_{ij} and s''_{ij} exist and attempt to demonstrate they must be the same solution. The difference between these solutions $s_{ij} = s'_{ij} - s''_{ij}$ must therefore satisfy the equations of equilibrium with zero body forces and zero boundary conditions. In linear elasticity the proof is very simple when one postulates a positive definite strain energy [22-24]. For linear viscoelasticity, the proof is quite lengthy and detailed. For the non-linear constitutive equation proposed in this thesis, which contains linear elasticity and linear viscoelasticity as special cases, the proof appears beyond the scope of this thesis. Intuitively the uniqueness seems obvious as zero forces and displacements on the boundary imply no internal forces or displacements from physical reasoning. In addition the homogeneity of the constitutive law guarantees zero output for zero input. To demonstrate this with mathematical rigor however is very difficult if not impossible except perhaps in very restrictive cases. One possible means of proving uniqueness is by using an extension to Eulers theorem for homogeneous functions [35] which has been developed by M. Freda [34].

IX. MATERIAL CHARACTERIZATION PROCEDURES

In the previous sections it has been demonstrated that homogeneous constitutive equations are characteristic of certain materials and even though the equations are non-linear they can often admit linear solutions. The problem with characterizing these non-linear time dependent materials is that it becomes a type of complex curve fitting exercise. When the functional form is expanded as was done by Rivlin, a fairly general characterization scheme can be worked out for the case when the kernel functions are reduced to product functions of time alone [44,52,62]. Lockett [62] has demonstrated how the characterization procedure can be carried out to yield approximations to the twelve kernel functions appearing in the first three integrals. Although the constitutive equations proposed in this thesis outwardly contain only single integrals, the kernel functions are homogeneous functionals of degree zero of the invariant histories. Since the forms of these kernels has not been specified, the characterization process could be much more complex than that proposed by Lockett. In this unspecified form, the kernels would be difficult if not impossible to determine. Simplifications can be made to approximate their general behavior and characterizations can be carried out. The characterization scheme described below appears to work quite well for composite solid propellants. Extensions of this method could be applied to other materials. For simplicity it will be assumed that the kernel functions are of the type that will admit linear solutions and that the only problems of interest are proportional problems. With these

restrictions the constitutive equation homogeneous to degree one can be expressed as

$$S_{ij}(x_k,t) = \delta_{ij} \int_0^t K_0\left[\overset{t}{\underset{0}{f(\xi)}},t-\tau\right] \dot{e}_{ii}(x_k,\tau)d\tau +$$

$$\int_0^t K_1\left[\overset{t}{\underset{0}{f(\xi)}},t-\tau\right] \dot{e}_{ij}(x_k,\tau)d\tau \qquad (9.1)$$

This equation is composed of two parts, a shear term and a primarily dilatational term. For simple shear the equation reduces to

$$S_{ij}(x_k,t) = \int_0^t K_1\left[\overset{t}{\underset{0}{f(\xi)}},t-\tau\right]\dot{e}_{ij}(x_k,\cdot)d\tau \ , \quad i \neq j. \qquad (9.2)$$

For purely dilatational deformations the equation reduces to

$$S_{ii}(x_k,t) = \int_0^t \left\{3K_0\left[\overset{t}{\underset{0}{f(\xi)}},t-\tau\right] + K_1\left[\overset{t}{\underset{0}{f(\xi)}},t-\tau\right]\right\} \dot{e}_{ii}(x_k,\tau)d\tau =$$

$$\int_0^t K_2\left[\overset{t}{\underset{0}{f(\xi)}},t-\tau\right]\dot{e}_{ii}(x_k,\tau)d\tau \ . \qquad (9.3)$$

Hence by characterizing the behavior in pure dilatational and pure shear tests, the total behavior under combined loadings can be determined. The method described below is applicable toward approximating either kernel function. However, since they are of identical form, only the shear case will be discussed below.

As an approximation to the behavior, the kernel functions can be expanded in a product series of the form

$$K_1\left[\overset{t}{\underset{0}{f(\xi)}}, t-\tau\right] = \sum_{i=1}^{N} G_i\left[\overset{t}{\underset{0}{f(\xi)}}\right] k_i(t-\tau) \ ,$$

where $$G_i\left[a\overset{t}{\underset{0}{f(\xi)}}\right] = G_i\left[\overset{t}{\underset{0}{f(\xi)}}\right] \ . \tag{9.4}$$

To demonstrate the difficulty in characterizing non-linear materials, only the first two terms in this expansion will be used. Substituting equation (9.4) into the shear constitutive equation produces

$$S_{12}(x_k,t) = G_1\left[\overset{t}{\underset{0}{f(\xi)}}\right] e_{12}(x_k,t) + \int_0^t k_1(t-\tau)\dot{e}_{12}(x_k,\tau)d\tau \tag{9.5}$$

Since the characterization is restricted to proportional tests, tests having physically homogeneous strain fields can be used where the strain input is then given by

$$e_{12}(x_k,t) = e_{12}(t) = f(t) \ . \tag{9.6}$$

Equation (9.5) now reduces to

$$S_{12}(t) = G_1\left[\overset{t}{\underset{0}{f(\xi)}}\right] f(t) + \int_0^t k_1(t-\tau)\dot{f}(\tau)d\tau \tag{9.7}$$

Equation (9.7) can be looked upon as containing a permanent memory term and a fading memory term. Tests that will separate these two effects now need to be determined. The simplest of such tests is the step strain, or ramp strain relaxation tests. For a jump strain of magnitude $\overset{\circ}{e}_{12}$ applied at time zero, an expression for the relaxation modulus is obtained.

$$E_r(t) = \frac{S_{12}(t)}{\overset{\circ}{e}_{12}} = G_1\left[\overset{t}{\underset{0}{u(\xi)}}\right] + k_1(t) \; , \qquad (9.8)$$

where $u(\xi)$ is the unit step function.

For a beginning the special cases when $G_1[\overset{t}{\underset{0}{f(\xi)}}]$, or $k_1(t-\tau)$ are zero will be considered. The first case is trivial as the equation reduces to linear viscoelasticity. The second case reduces to a time dependent permanent memory equation.

$$S_{12}(t) = G_1\left[\overset{t}{\underset{0}{f(\xi)}}\right] e_{12}(t) \qquad (9.9)$$

In section 4 the application of the L^P norms in permanent memory constitutive theory was demonstrated. A logical choice of the characterization of $G_1[\overset{t}{\underset{0}{f(\xi)}}]$ is therefore L^P norms of $f(\xi)$. Since the functional is homogeneous to degree zero it must be expressable as a ratio of norms. Relaxation behavior for most materials can be described by a power law representation

$$E_r(t) = a_1 t^{-n_1} + a_2 t^{-n_2} + \cdots = G_1\left[\overset{t}{\underset{0}{u(\xi)}}\right] \qquad (9.10)$$

A logical choice for the functional would therefore be

$$G_1\left[\overset{t}{\underset{o}{f(\xi)}}\right] = a_1\left(\frac{||f||_{p_1}}{||f||_{q_1}}\right)^{r_1} + a_2\left(\frac{||f||_{p_2}}{||f||_{q_2}}\right)^{r_2} + \cdots ,$$

$$\text{where } p_i > q_i, \text{ and } r_i\left(\frac{1}{p_i} - \frac{1}{q_i}\right) = -n_i \; . \tag{9.11}$$

For a jump strain, equation (9.11) reduces identically to the power law representation given for $E_r(t)$ in equation (9.10). The problem is then reduced to determining r_i, p_i, q_i assuming all the a_i and n_i are known from curve fitting the relaxation data.

For a constant strain rate test the output can be shown to be

$$S_{12}(t) = \dot{e}_{12}(t)G_1\left[f(\xi)\right] = e_{12}(t)\left\{a_1c_1t^{-n_1} + a_2c_2t^{-n_2} + \cdots\right\} ,$$

$$C_i = (1 + q_i)^{r_i/q_i} \Big/ (1 + p_i)^{r_i/p_i} \; . \tag{9.12}$$

By fitting this data in an identical power series the coefficients C_i can be determined. There now exists two equations in each of the three unknowns, p_i, q_i, r_i. Hence one more test condition will provide the necessary equation. Since propellant materials appear to be most sensitive to the maximum strain in their history, one could at this point simply choose $p_i = \infty$ and determine how well the results fit random inputs. Note how little one test result has to do with another for non-linear materials. If the material were linear,

all shear test results could be predicted simply by knowing the output to a jump input, as superposition is applicable. The simple case discussed above appears to fit most propellant data quite well.

To characterize the kernel functions when both fading and permanent memory behavior is present (admitting the first two terms only) can be a very complicated task as demonstrated above. In the theory of linear viscoelasticity the simple kernel function $k(t-\tau)$ is usually approximated by a Prony series [61] of the form

$$k(t) = \sum_{i=1}^{N} A_i \exp(-t/\gamma_i), \quad A_i, \gamma_i, \text{ constants} . \qquad (9.13)$$

In the Prony series representation the N relaxation times γ_i are picked using good judgement and the A_i are optimized using some form of linear regression analysis. Those terms having very small A_i can be discarded and perhaps new γ_i selected based on the first regression results and the process repeated using fewer terms until one is satisfied. Computer programs have been developed that actually perform all these calculations and yield optimum A_i and γ_i for an N term Prony series.

A similar procedure can be used in characterizing the non-linear but homogeneous constitutive equation of degree one. In the Prony series representation of linear viscoelasticity the γ_i are estimated and the A_i determined since attempting to determine the exponents is a non-linear problem and can lead to great difficulties. The same problem is present in attempting to determine the degree of the norms.

It is therefore recommended that a similar procedure be followed in characterizing these non-linear materials. The process given below is only valid for materials having homogeneous but non-linear constitutive equations. The homogeneity condition is very easily verified experimentally, as is the superposition principle. If the material obeys both the superposition and homogeneity conditions, it is linear and linear methods should be used as they are very simple.

For a general characterization procedure, it is suggested that the kernel functions be approximated as

$$K\left[\overset{t}{\underset{o}{f(\xi)}}, t-\tau\right] = \sum_{i=o}^{N}\sum_{j=o}^{N} A_{ij}\left(\frac{||f||_{p_i}}{||f||_{q_i}}\right)^{r_i} \exp[-(t-\tau)/\gamma_j] \ . \tag{9.14}$$

In the above equation the P_i, q_i, r_i and γ_j are estimated and the A_{ij} are determined by a regression analysis. However, unlike the linear constitutive law, where only the relaxation modulus or some other convenient test is used to determine the coefficients, for the non-linear material several different shear and dilatational tests must be used to determine the coefficients for their appropriate kernel functions. This can only be accomplished by substituting the expansion directly into the constitutive equation to obtain, for instance, a pure shear input.

$$S_{12}(t) = \sum_{i=o}^{N}\sum_{j=o}^{N} A_{ij}\left(\frac{||f||_{p_i}}{||f||_{q_i}}\right)^{r_i} \exp(-t/\gamma_j) \int_o^t \exp(\tau/\gamma_j)\dot{f}(\tau)d\tau. \tag{9.15}$$

Since the r_i, p_i, q_i, γ_j and strain input $f(\tau)$ are all known

this equation can be reduced to

$$S_{12}(t) = A_{ij}X_{ij}\left[\overset{t}{\underset{0}{f(\tau)}},p_i,q_i,r_i,\gamma_j,t)\right] ,$$

where X_{ij} is calculatable. (9.16)

Equation (9.16) is a linear equation in the A_{ij} and standard regression analysis procedures can be used to determine the coefficients. To accomplish this several different shear inputs, say $f_1, f_2,\cdots f_n$ must be used and each function $X_{ij}(f_n,t)$ must be evaluated at many times, say $(t_1, t_2,\cdots t_n)$. The experimental data from these various tests must be determined to yield the experimental values of the stress S_{12} for each input f_n at several times t_j. The resulting mass of data can then be analyzed using linear regression methods to determine the best values of A_{ij}. Computed values of the stress can then be compared to observed values to determine the accuracy of the method. To determine whether the constitutive law is of any value, it must accurately predict the results of tests not used in the characterization procedure. This test is the only test for the validity of a constitutive equation. If it cannot predict with reasonable accuracy it can lead to greatly erroneous results when used in stress analyses as six of the system of fifteen equations in fifteen unknowns used in structural analysis are constitutive equations.

9.1 Non-Linear Elasticity with Permanent Memory

Many materials exhibit the so-called time independent "Mullins' Effect". The effect is a stress-softening that appears only to depend on the magnitude of the strain history and not on time. Love [30] called this behavior "elastic hysteresis" and indicated it occurred in some metal wires. The process appears to be irreversible and in the limits of small strain is contained in the homogeneous constitutive equation of degree one. The problem is to express the history dependency without having time dependency. The behavior can be represented for proportional loading conditions by

$$S_{ij}(t) = \delta_{ij}K_1[(f(t)/||f||_\infty)^2]e_{ii}(t) + K_2[(f(t)/||f||_\infty)^2]e_{ij}(t) \tag{9.17}$$

This equation yields linear elastic response on the first stretch and a hysteresis response on any subsequent stretch. It contains no time effects, only history effects.

X. REALISTIC CHARACTERIZATION OF COMPOSITE PROPELLANTS

For nearly a decade composite solid propellant materials have for the most part been treated as linear viscoelastic materials. Today the propellant industry has the ability to perform complex thermoviscoelastic stress analysis using thermorheologically simple linear viscoelastic constitutive theory. Careful examination of propellant data however indicates the materials are not linear viscoelastic even at small strain. Researchers in the propellant industry have been applying incorrect criteria of linearity to their materials [1,2,19]. Assumptions have been made that if the material has a relaxation modulus that is independent of strain, then the material is linear. This assumption is not correct. Having a relaxation modulus that is strain independent is but a single check of the homogeneity condition and in no way checks the validity of the superposition principle which is the real test for linearity. Hence for over a decade complex computer analyses have been performed using linear viscoelastic theory yielding highly questionable results.

To demonstrate that propellants are non-linear materials even at small strains, one need only check the superposition principle experimentally. In the range of small strains below detectable de-wetting or volumetric dilatation [9-11], most propellants have a relaxation modulus independent of strain and in general closely obey the scalar multiplication homogeneity rule. Yet this relaxation modulus cannot be used to accurately predict the response due to other isothermal, low rate, small strain inputs. To demonstrate the inadequacies of

linear viscoelastic predictions on solid propellants, laboratory tests where superposition is applicable can be performed. Figure 10.1 illustrates the stress-strain-dilatational behavior of a typical composite propellant. The dilatation-strain behavior is caused by vacuole formation within the microstructure [9-11] and causes a stress-softening; an obvious type of non-linearity. Below significant dilatation the material appears to have a relaxation modulus that is independent of strain as illustrated in figure 10.2. To determine if superposition is applicable, the interrupted ramp-strain stress relaxation test can be employed. Linear viscoelastic theory would predict the stress output for the second loading would be simply the superposition of the initial response with the continuation of the original stress-relaxation response. Figure 10.3 illustrates the linear viscoelastic prediction and the actual experimental results for this interrupted ramp strain test. From this and other tests it is apparent errors of over plus or minus one hundred percent are typical when linear viscoelastic theory is used to predict the response of propellant materials. To clarify the point, the data in figure 10.3 are plotted stress against strain in figure 10.4. Here it is apparent that when the straining is again commenced, the response rapidly rejoins the original constant rate response, whereas the linear theory would indicate it should parallel the original response. Figure 10.5 illustrates similar test results for the doubly interrupted ramp test plotted stress vs strain. Again the same behavior of rejoining the original constant rate response is shown and also that the errors

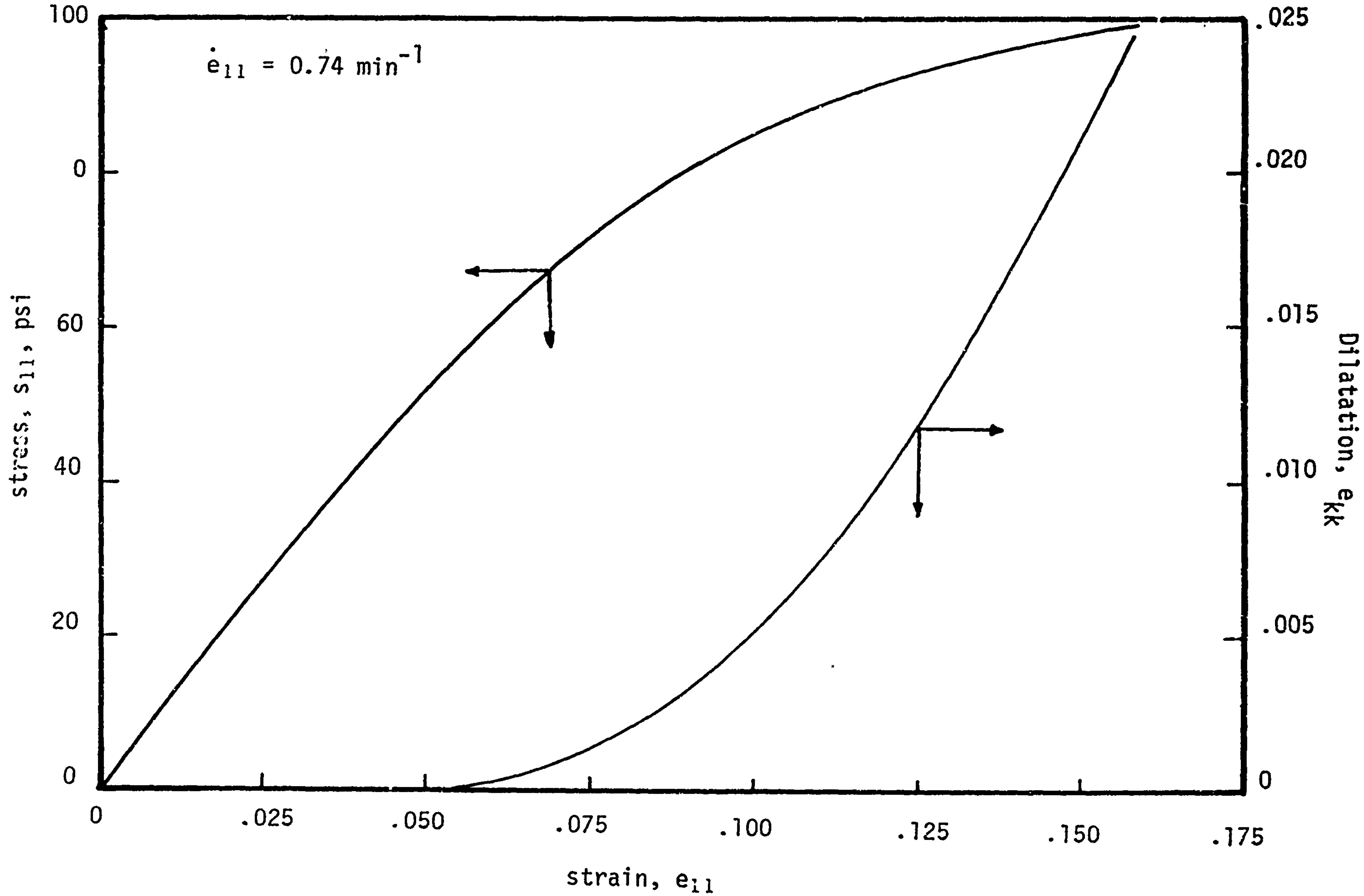
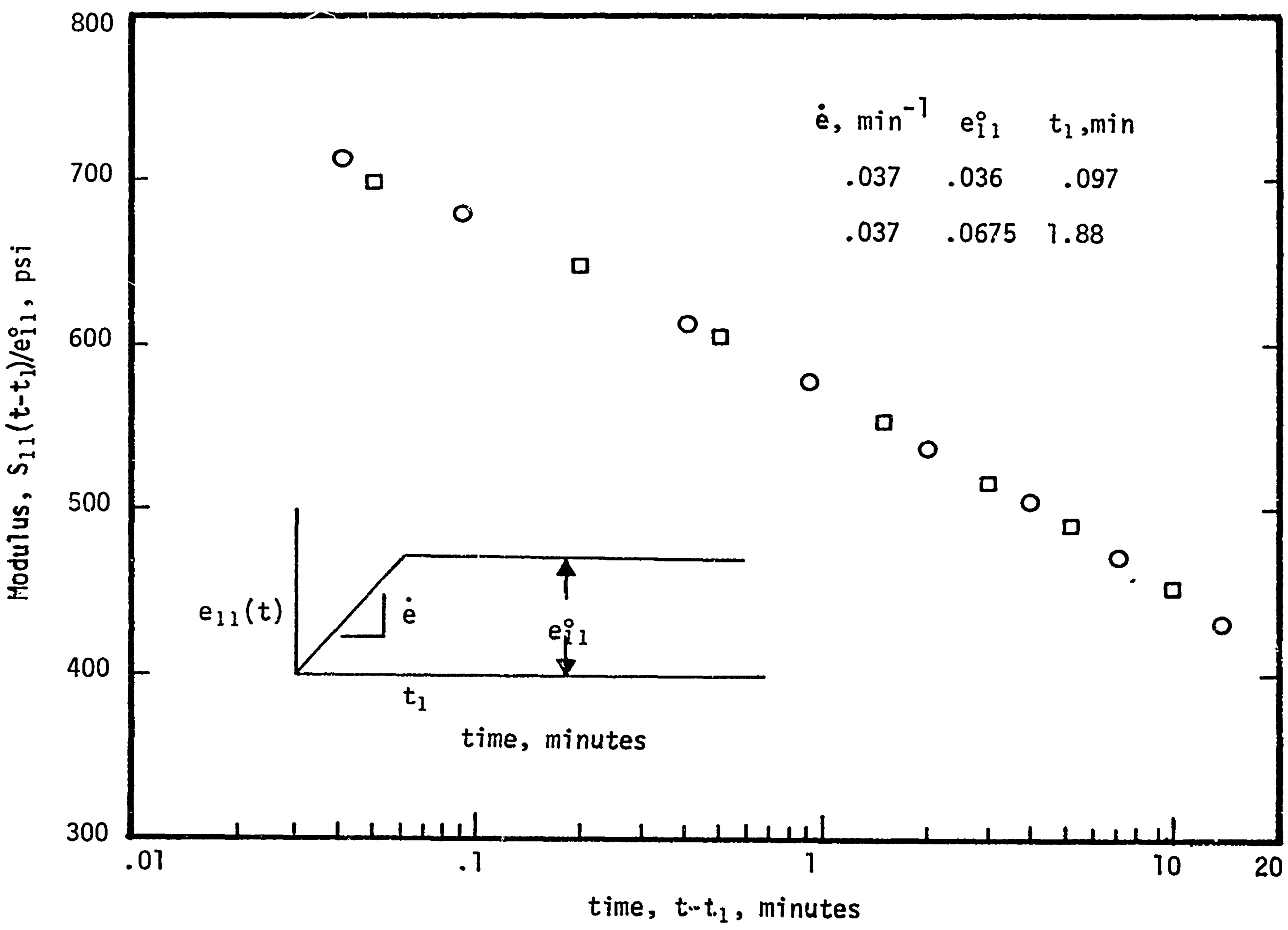


Figure 10.1. UNIAXIAL STRESS-STRAIN AND DILATATION-STRAIN BEHAVIOR OF A COMPOSITE PROPELLANT.



10.2. RAMP RELAXATION MODULUS FOR TWO SAMPLES TESTED AT DIFFERENT STRAIN LEVELS

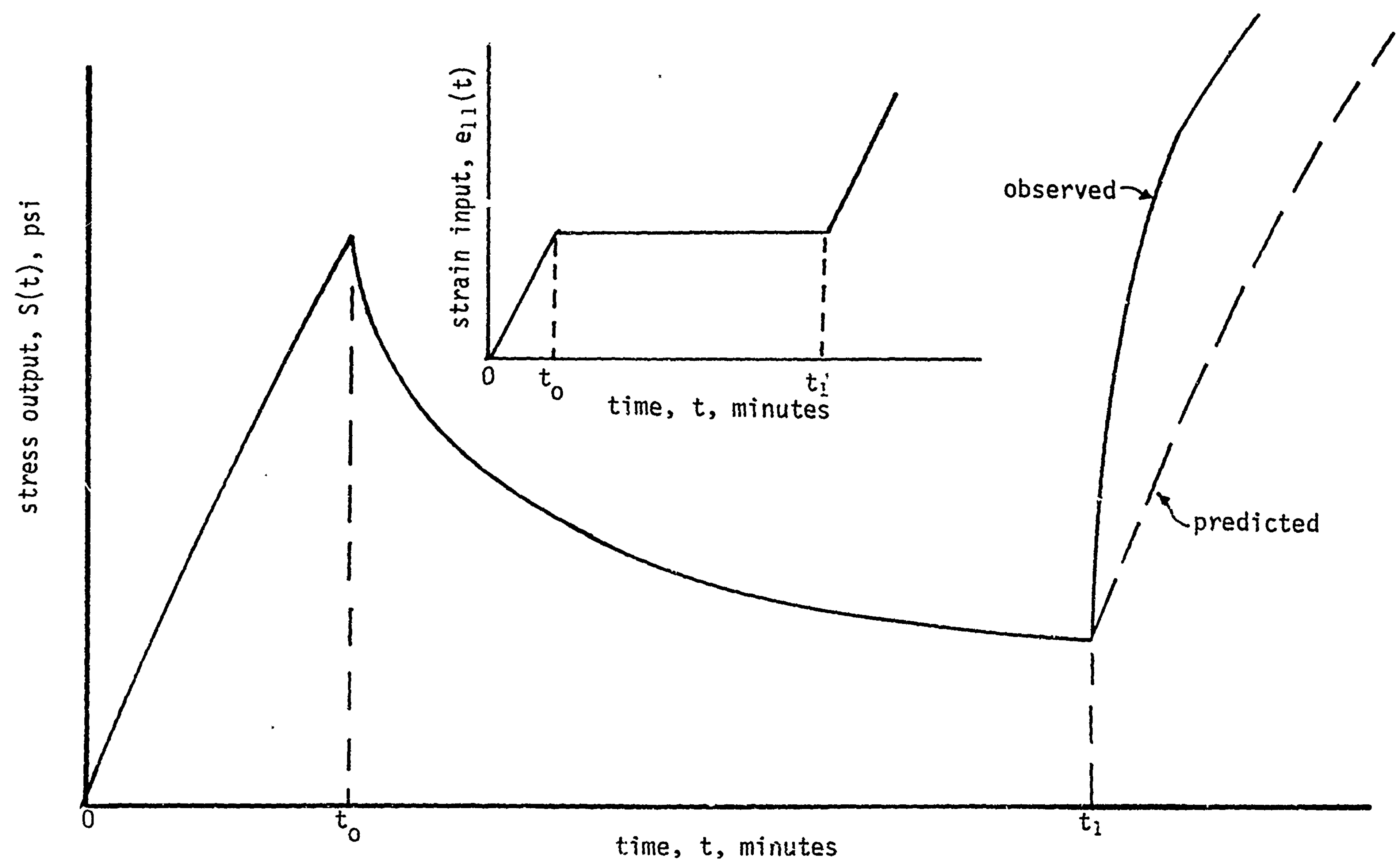


Figure 10.3. LINEAR VISCOELASTIC STRESS-TIME PREDICTIONS AND EXPERIMENTAL DATA FOR AN INTERRUPTED RAMP STRAIN INPUT ON A TYPICAL COMPOSITE PROPELLANT.

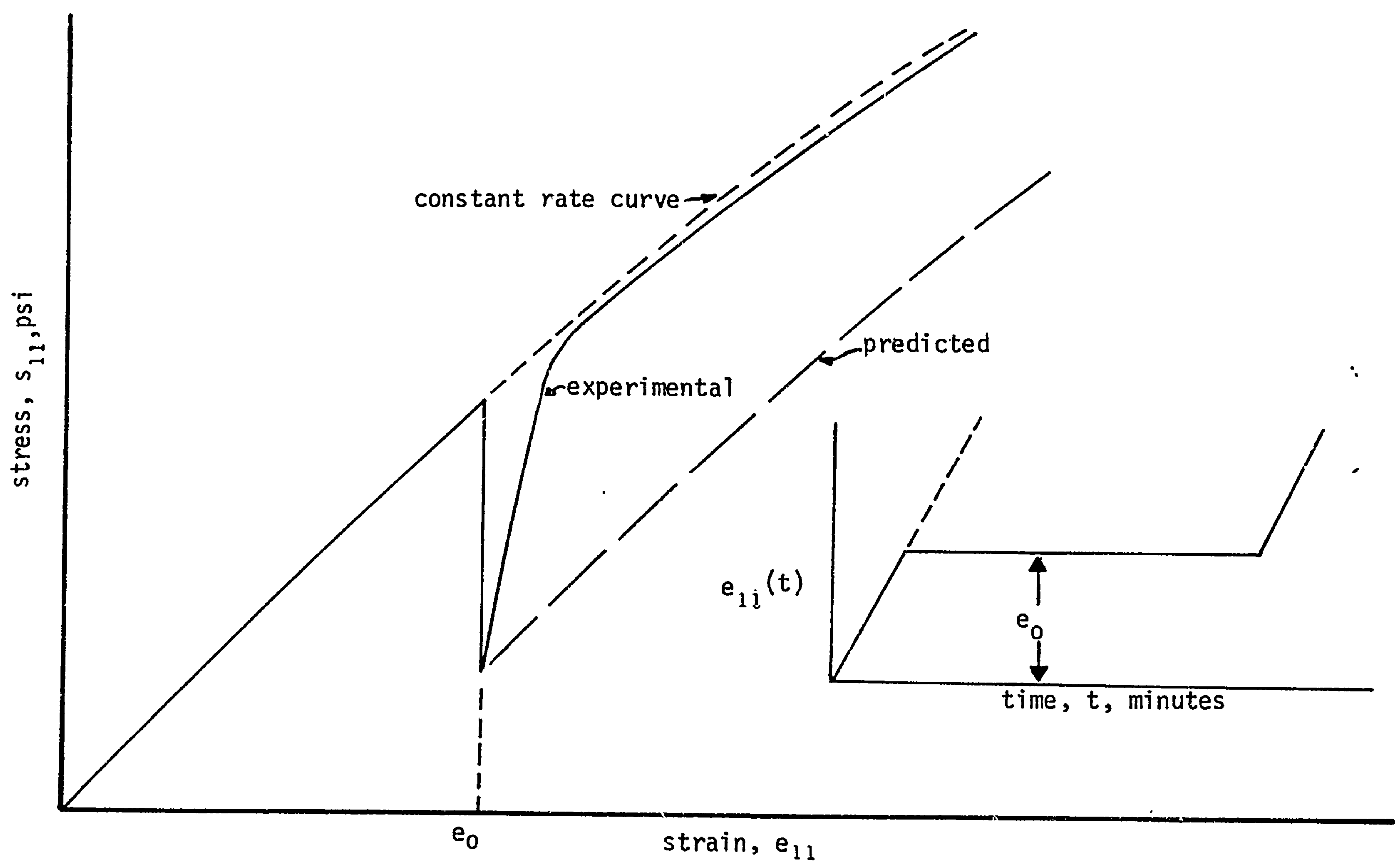


Figure 10.4. LINEAR VISCOELASTIC STRESS-STRAIN PREDICTION AND EXPERIMENTAL DATA FOR AN INTERRUPTED RAMP STRAIN INPUT ON A TYPICAL COMPOSITE PROPELLANT.

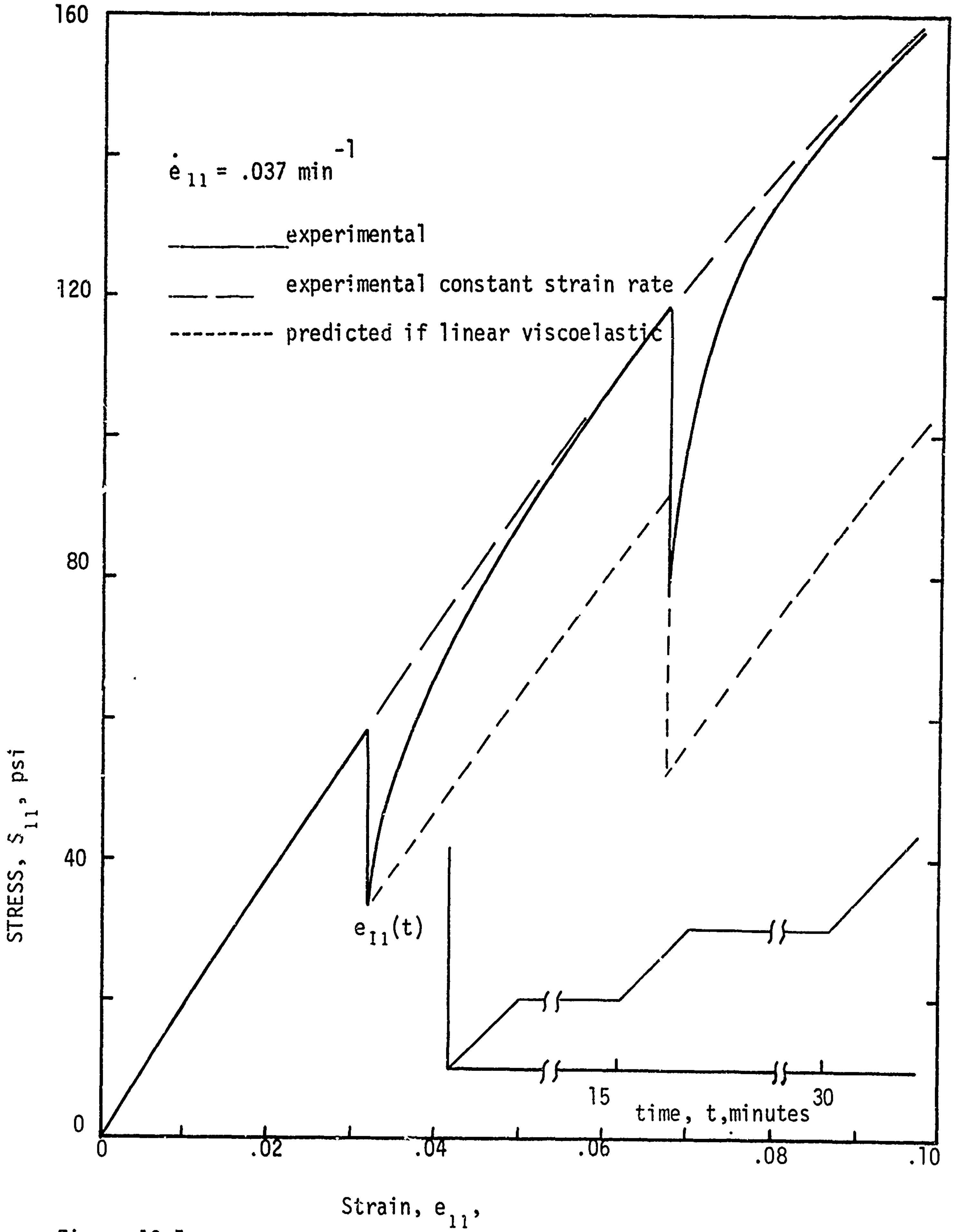


Figure 10.5.
STRESS OUTPUT FOR INTERRUPTED CONSTANT STRAIN RATE TEST.

of linear theory grow with each cycle. Plotting the relaxation data from each portion of this test in figure 10.6 further demonstrates that the relaxation responses for the first and second straining are identical when time is measured from the beginning of each relaxation. Interestingly enough this means that part of the memory of its past has somehow been completely annihilated and that the previous relaxation history has had no influence on the second relaxation. This is not fading memory response since all of the past has not been forgotten. It does however indicate that the fading memory portion of the viscoelastic constitutive equation is for all practical purposes zero as long as the strain is increasing.

In figure 10.7 further verification of the homogeneity principle for these materials is presented. In this figure the stress output is compared for two cyclic inputs that differ in amplitude only. As dictated by the homogeneity principle, these data indicate that the ratio of the stress outputs is equal to the ratio of amplitudes of the cyclic strain inputs. The data in figure 10.8 compares the linear-viscoelastic prediction for the cyclic data presented in figure 10.7. The agreement between the linear predictions and the experimental data are quite good for this test whereas it was found to be poor for the tests discussed earlier in this section. Good agreement between experimental data and linear predictions might be expected for some tests since the material has been shown to satisfy one of the conditions of linearity. Furthermore the dilatation data on propellants in this range of small strains prior to dewetting indicate near

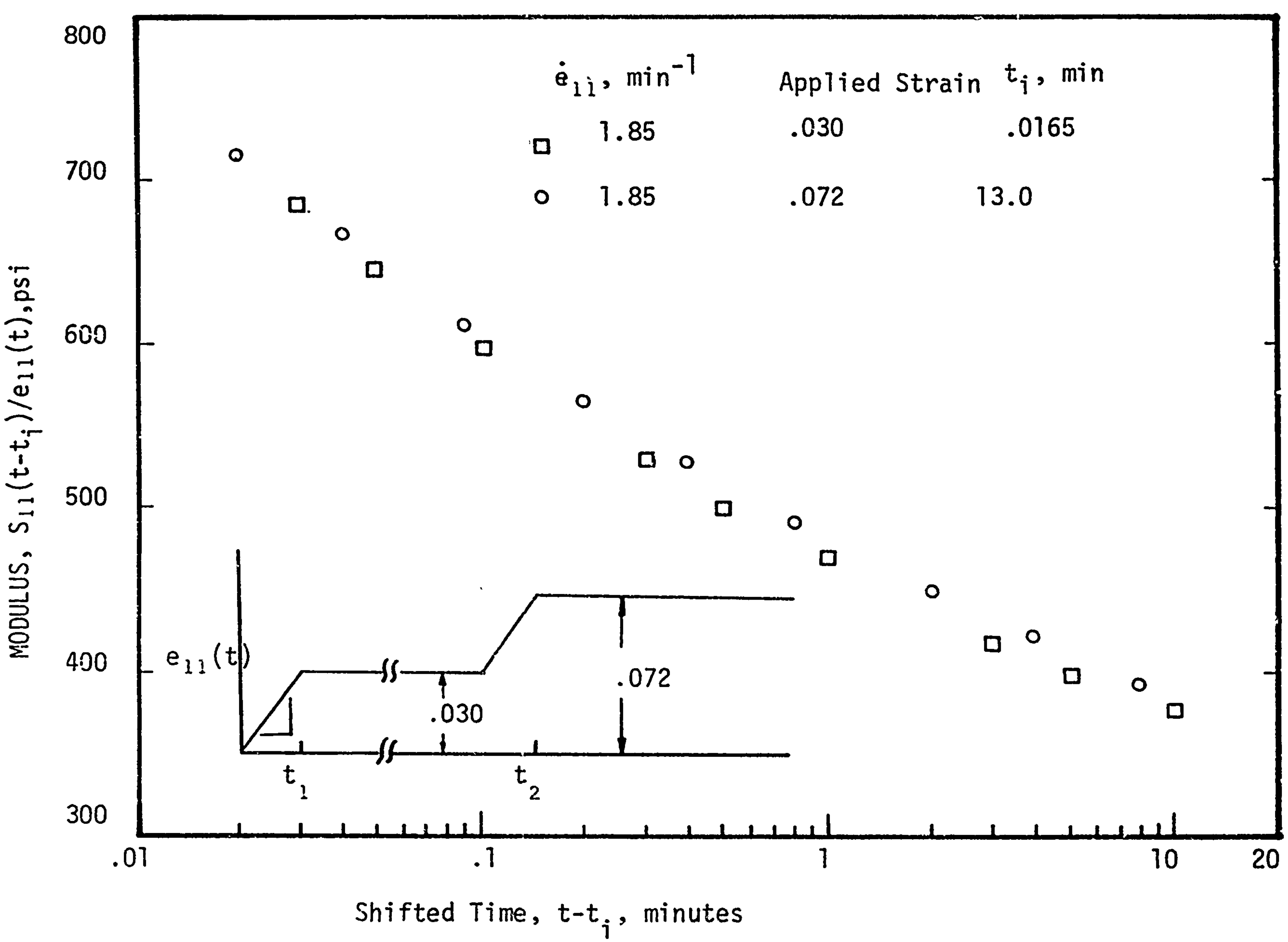


Figure 10.6. RAMP RELAXATION MODULUS FOR ONE SAMPLE TESTED AT TWO DIFFERENT STRAIN LEVELS.

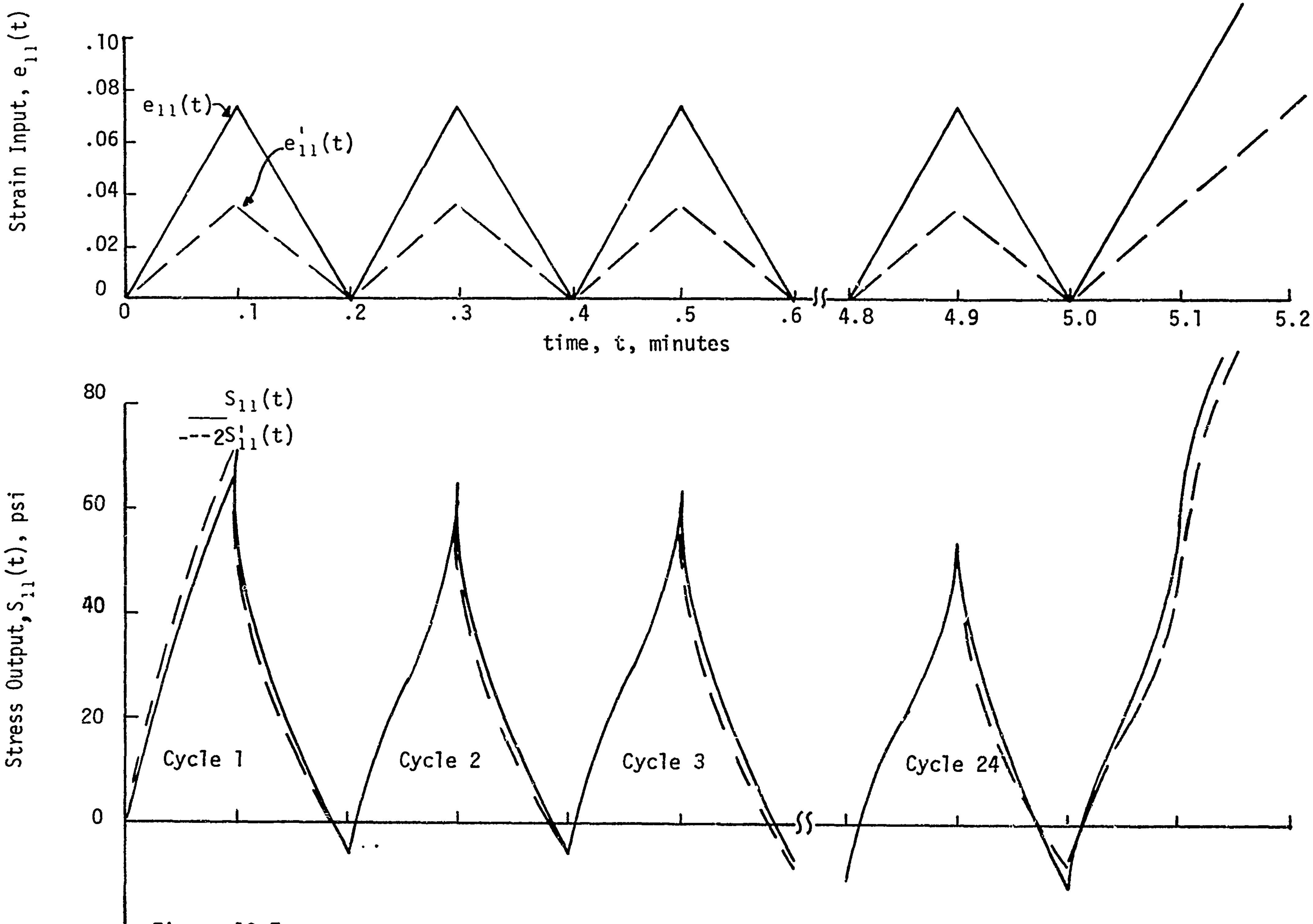


Figure 10.7.
VERIFICATION OF HOMOGENEITY PRINCIPLE FOR A CYCLIC STRESS INPUT.

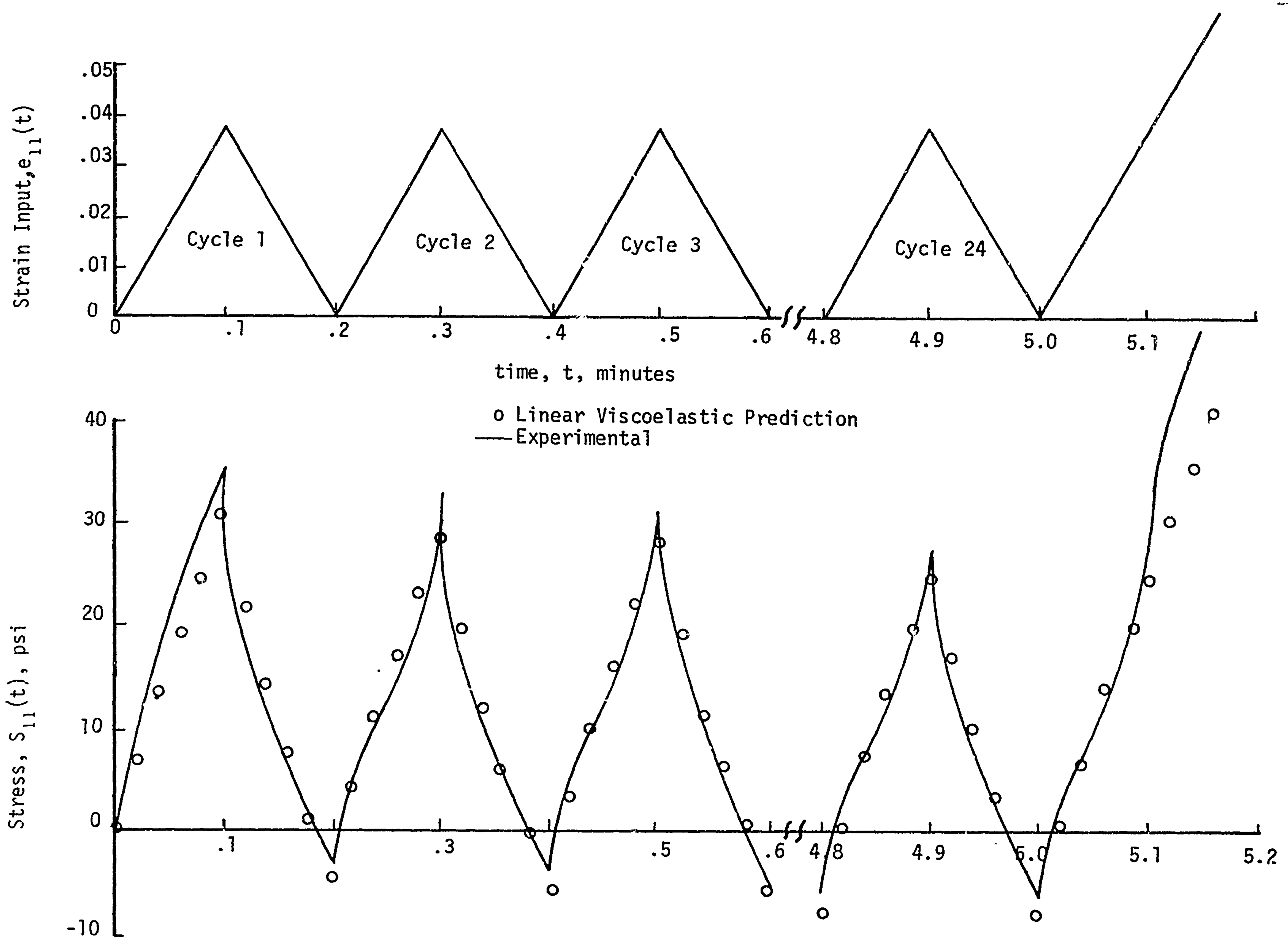


Figure 10.8. COMPARISON OF LINEAR VISCOELASTIC PREDICTION AND EXPERIMENTAL DATA FOR A CYCLIC STRAIN INPUT.

incompressible elastic behavior [9-11]. Incorporating these features into the constitutive equation indicate a valid form would be

$$S_{ij}(t) = \delta_{ij}P + G\left[\overset{t}{\underset{o}{f(\xi)}}\right] e_{ij}(t) ,$$

where p is an arbitrary pressure. (10.1)

The relaxation data for most propellants obeys a simple power law expression as indicated by these data when plotted logarithmically in figure 10.9. From the previous discussion in section 9 dealing with material characterization a logical choice for the functional is

$$G\left[\overset{t}{\underset{o}{f(\xi)}}\right] = \sum_{i=o}^{N} A_i \left(\frac{||f||_{p_i}}{||f||_{q_i}}\right)^{r_i} ,$$

$$\text{where } r_i\left(\frac{1}{p_i} - \frac{1}{q_i}\right) = - n . \qquad (10.2)$$

For a jump strain equation (10.2) then reduces to

$$G\left[\overset{t}{\underset{o}{u(\xi)}}\right] = E_r(t) = kt^{-n} = t^{-n} \sum_{i=o}^{N} A_i \qquad (10.3)$$

To complete the characterization process we need only determine A_i, p_i, q_i, and r_i. The complex characterization procedure discussed in the previous section was not used for this purpose. Instead only one term was taken choosing $p_1 = \infty$, $A_1 = k$ and graphically determining r_1 and q_1 to fit a few tests. The results of this very simple

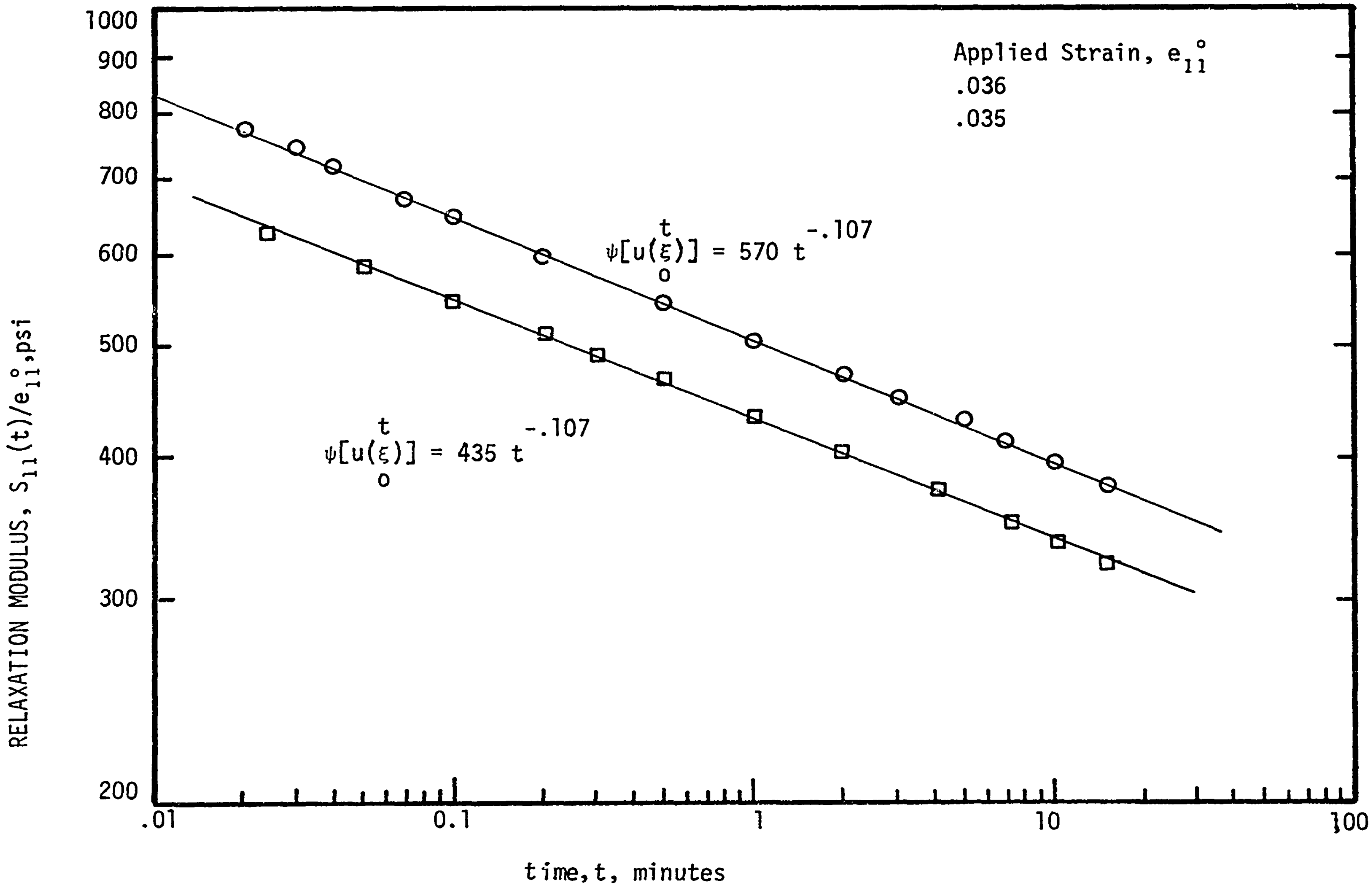


Figure 10.9 STRESS OUTPUT TO A RAPIDLY APPLIED CONSTANT STRAIN INPUT

analysis is demonstrated in figures 10.10 through 10.12 which compare calculated and observed response for several tests plotted both stress-time and stress-strain. The close agreement between experiment and theory for this single term representation would appear to indicate this is a powerful method of characterization and valid for propellant materials. However comparing the predictions with the actual data for the cyclic tests, figures 10.13 and 10.14, shows the agreement is not so good as demonstrated in the previous figures. The reason for this disagreement between prediction and observation lies in the need to have some fading memory viscoelasticity present, since compressive stresses for the state of positive tensile strain cannot come from the permanent memory portion of the constitutive equation. Proper characterization procedures will bring out such defects in the chosen representation.

In an attempt to improve the characterization process a three term expansion was chosen as suggested by the discussion in section 9. Instead of using exponential terms however a single power of t was chosen. The constitutive equation chosen has the form

$$S_{ij}(t) = \delta_{ij}P + A_1\left(\frac{|f|}{||f||_{q_1}}\right)^{r_1} e_{ij} + A_2\int_0^t (t-\tau)^{-n_2}\,\dot{e}_{ij}(\tau)d\tau$$

$$+ A_3\left(\frac{|f|}{||f||_{q_3}}\right)^{r_3}\int_0^t (t-\tau)^{-n_3}\,\dot{e}_{ij}(\tau)d\tau \ ,$$

where P = arbitrary pressure, and

$|\cdot|$ = absolute value. (10.4)

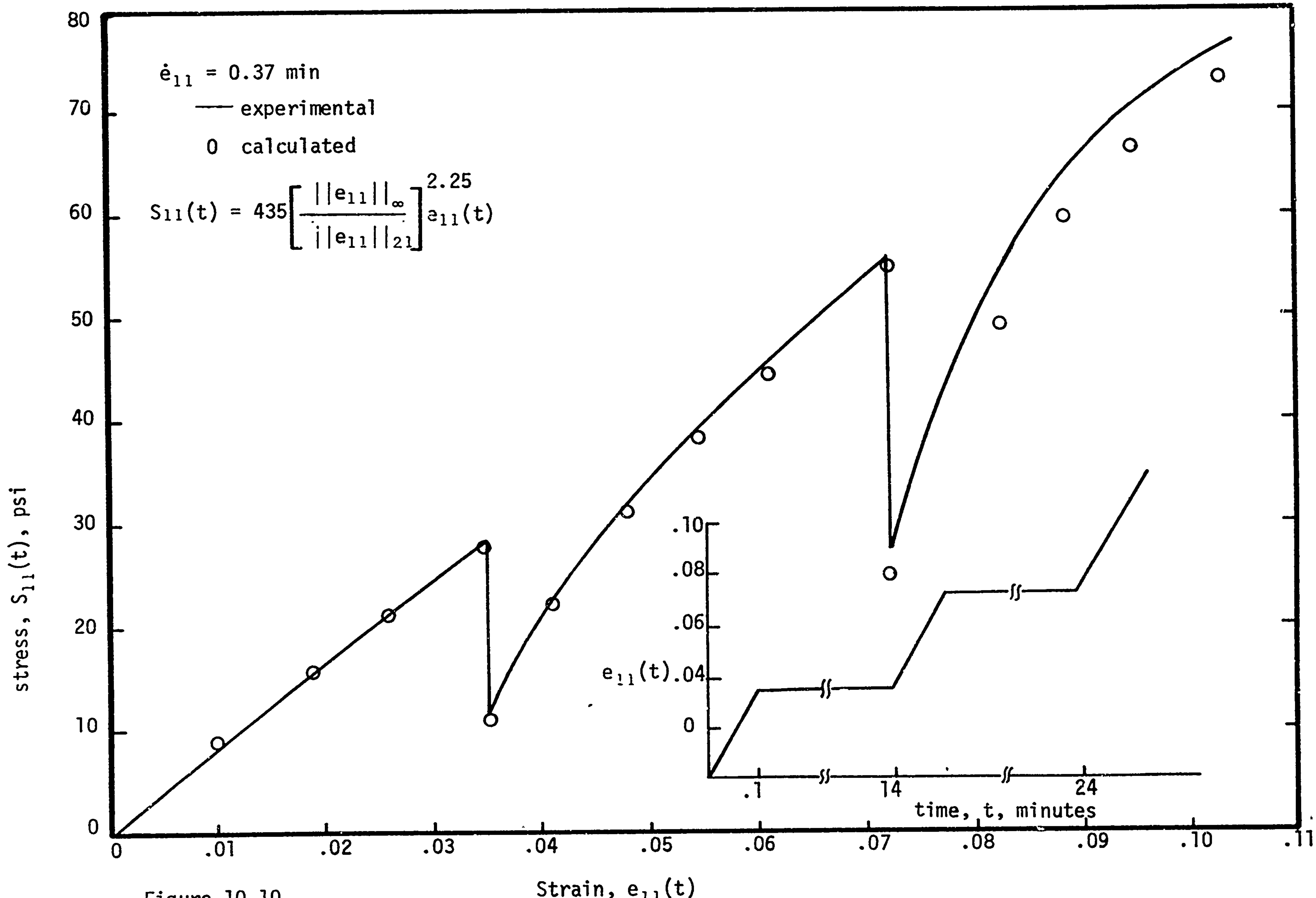


Figure 10.10.
COMPARISON OF CALCULATED AND OBSERVED STRESS-STRAIN OUTPUT FOR AN INTERRUPTED RAMP STRAIN INPUT

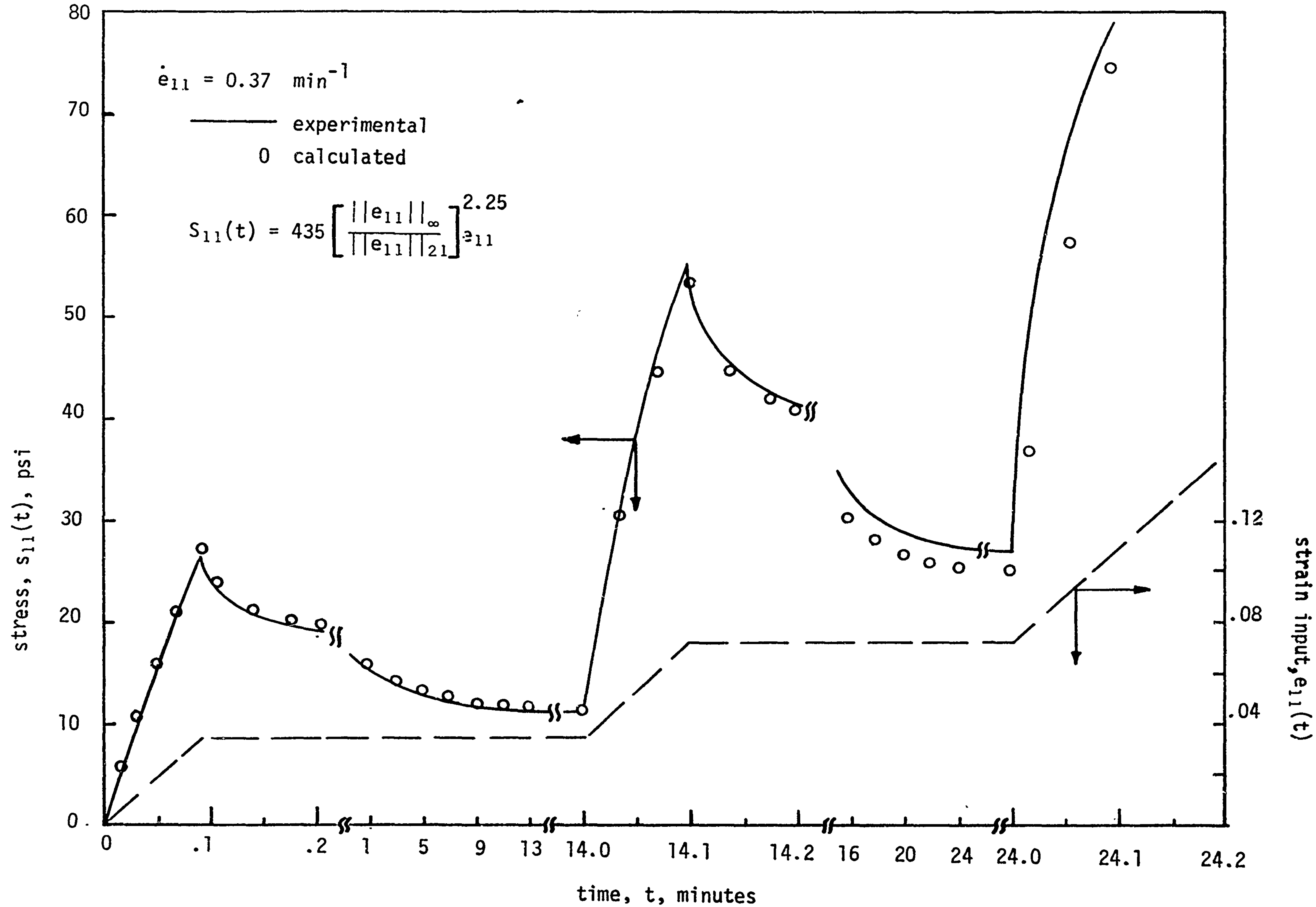


Figure 10.11. COMPARISON OF CALCULATED AND OBSERVED STRESS-TIME OUTPUT FOR AN INTERRUPTED RAMP STRAIN INPUT.

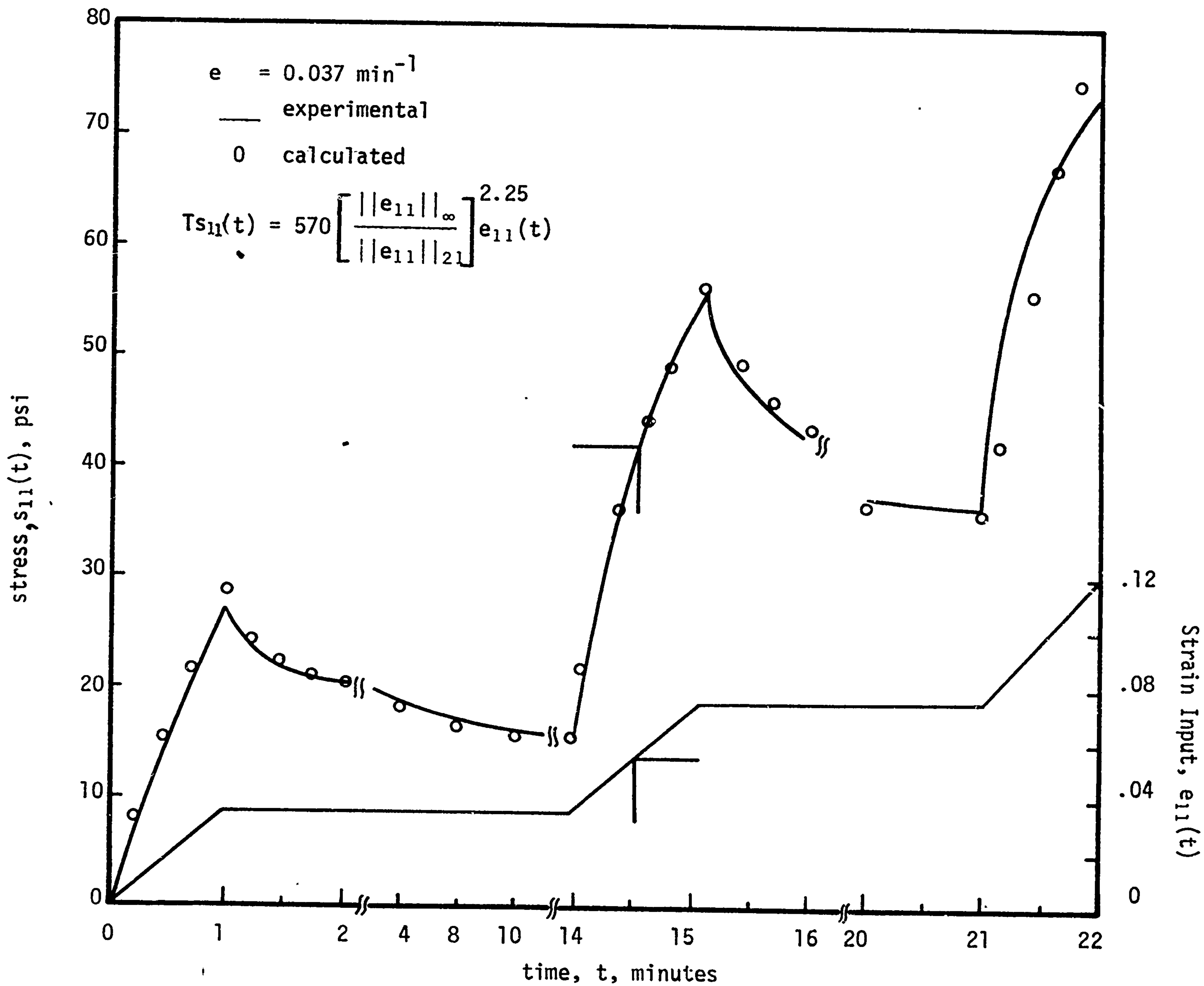


Figure 10.12. COMPARISON OF CALCULATED AND OBSERVED STRESS-TIME OUTPUT TO AN INTERRUPTED RAMP STRAIN INPUT

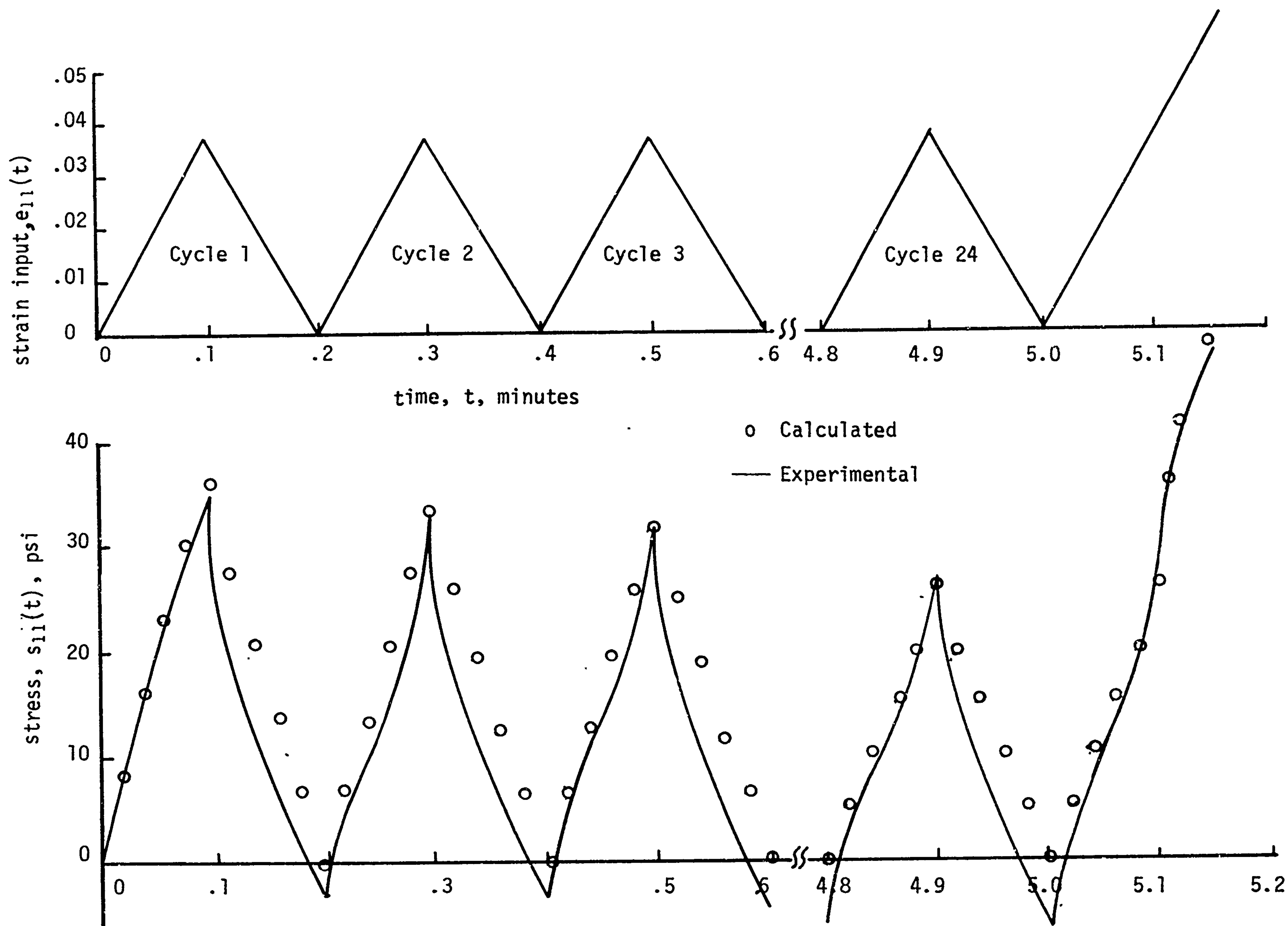


Figure 10.13. COMPARISON OF EXPERIMENTAL AND CALCULATED STRESS OUTPUT FOR A CYCLIC STRAIN INPUT.

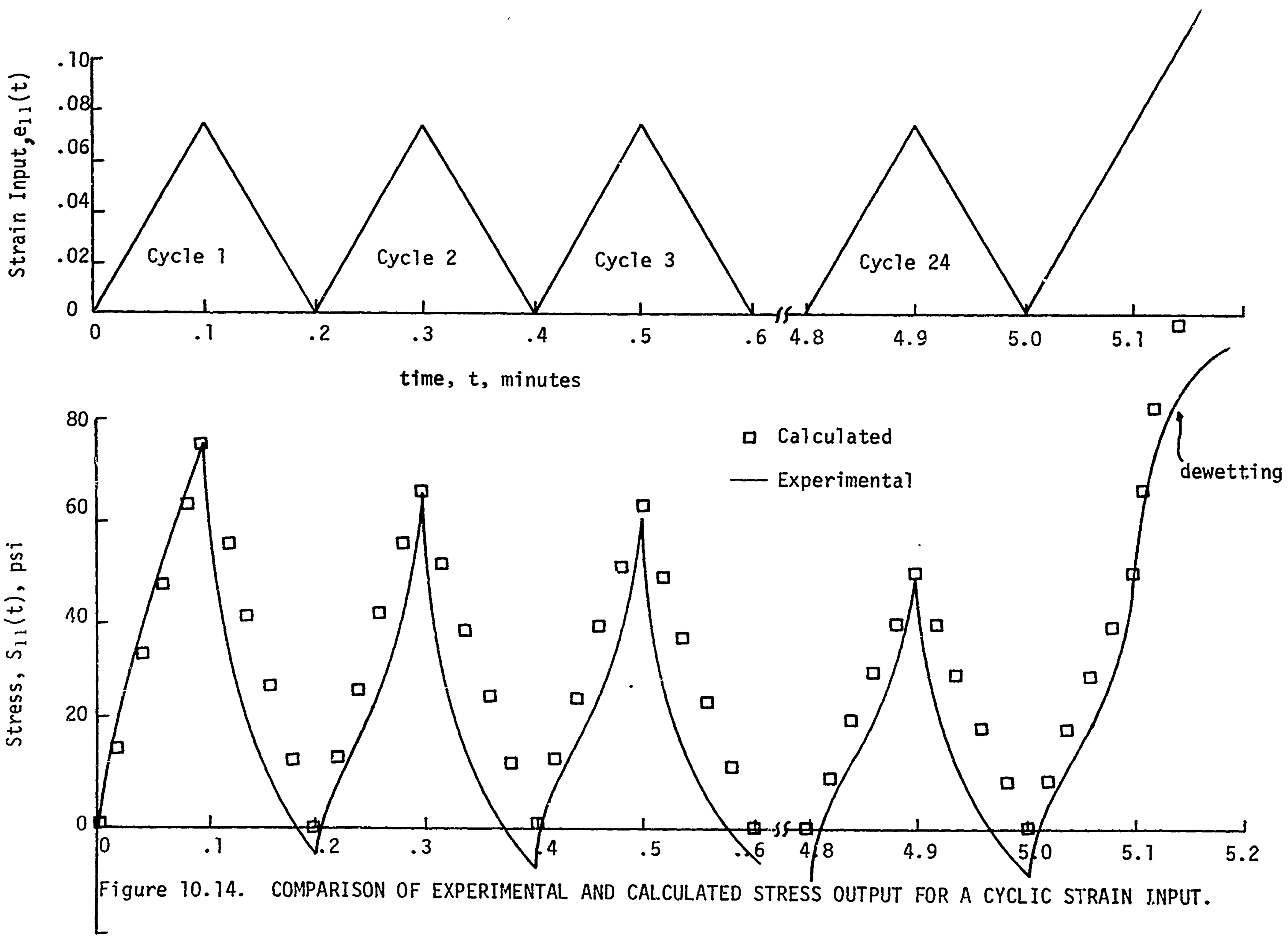


Figure 10.14. COMPARISON OF EXPERIMENTAL AND CALCULATED STRESS OUTPUT FOR A CYCLIC STRAIN INPUT.

A simple analysis of all the test data indicate that the material would be well characterized if the parameters in the equation took on the following values

$$n_2 = n_3 = 0.1$$
$$r_1 = 2.25$$
$$r_3 = 1.0$$
$$q_1 = 21$$
$$q_3 = \infty$$
$$A_1 = A_2 = - A_3 = 570$$

Substituting these values into equation (10.4) and rearranging terms yields

$$S_{ij}(t) = \delta_{ij}P + 570\left(\frac{|f|}{||f||_{21}}\right)^{2.25} e_{ij}(t) + + 570\left[1 - \frac{|f|}{||f||_{\infty}}\right]\int_0^t (t-\tau)^{-.1}\,\dot{e}_{ij}(\tau)d\tau \; . \qquad (10.5)$$

For tests where the strain is never decreasing (or never increasing), such as those illustrated in figures 10.10 through 10.12, the last term in equation (10.5) contributes nothing since for these tests $|f|$ equals $||f||_{\infty}$. The data in figures 10.10 through 10.12 calculated by equation (10.5) and that calculated by equation (10.1) is therefore identical. Comparisons between the calculated and observed data for the cyclic strain inputs is illustrated in figures 10.15

and 10.16. As seen by the data illustrated in these figures, the calculated and experimental data agree quite well. Perhaps other inputs exist, where again the agreement of even this modified constitutive equation will predict poorly. The only way to be assured a non-linear constitutive equation will predict accurately is to perform all possible tests and compare. Naturally this is impossible, however the least one should do is use a large number of greatly different tests. Inputs of a similar type to those the material in question will be subjected to in its lifetime, performed at the same temperatures and over the same time scales should be used in realistic characterization procedures.

In particular there are two things a rheologist attempting to mathematically describe the behavior of materials should always remember.

1) Simply because the chosen representation accurately curve fits the tests used in the characterization procedure does not guarantee accurate predictions for other different tests.

2) If a constitutive equation cannot predict the output to an arbitrary input, it is of little value in general stress analysis.

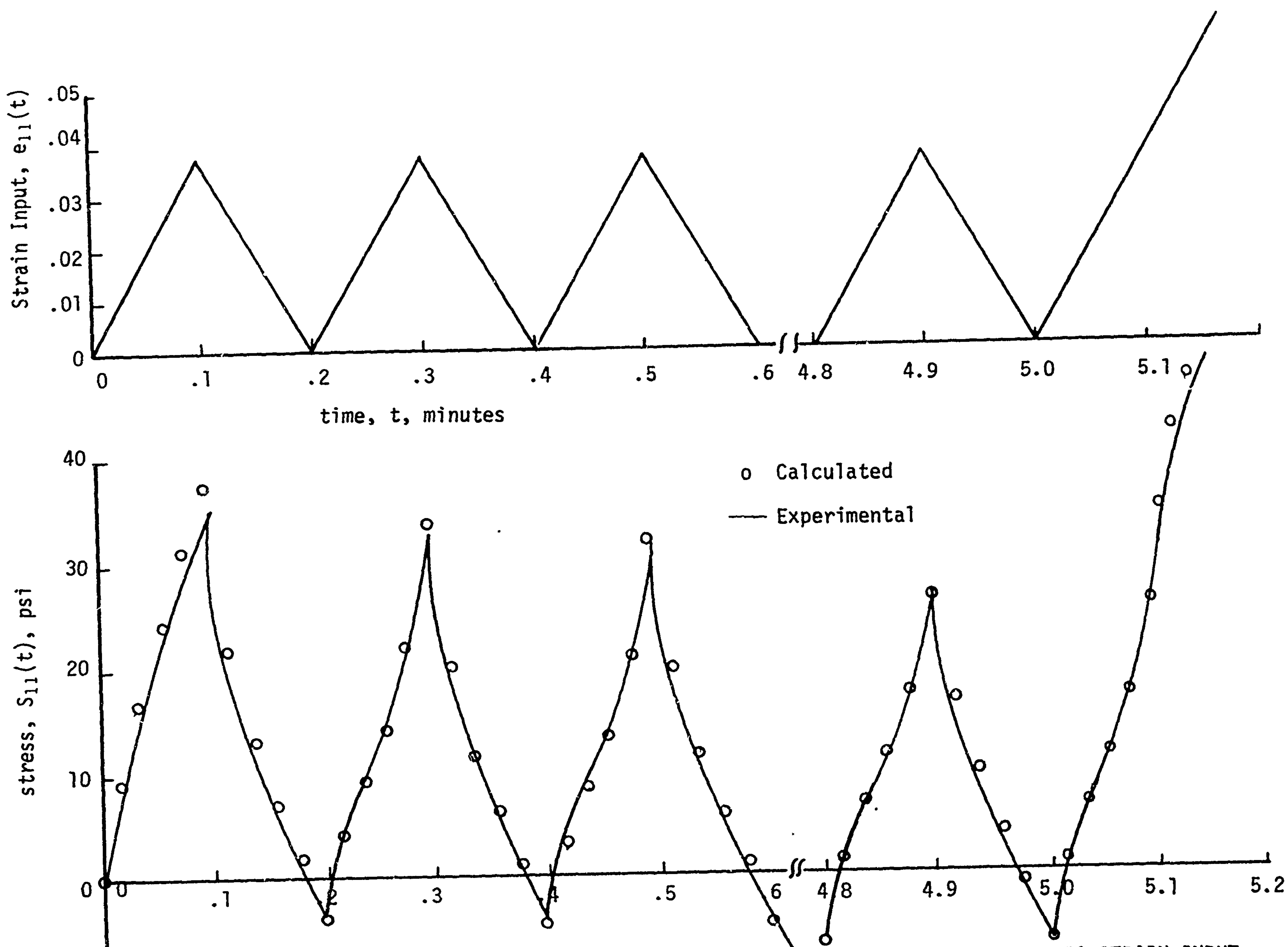


Figure 10.15. COMPARISON OF EXPERIMENTAL AND CALCULATED STRESS OUTPUT FOR A CYCLIC STRAIN INPUT

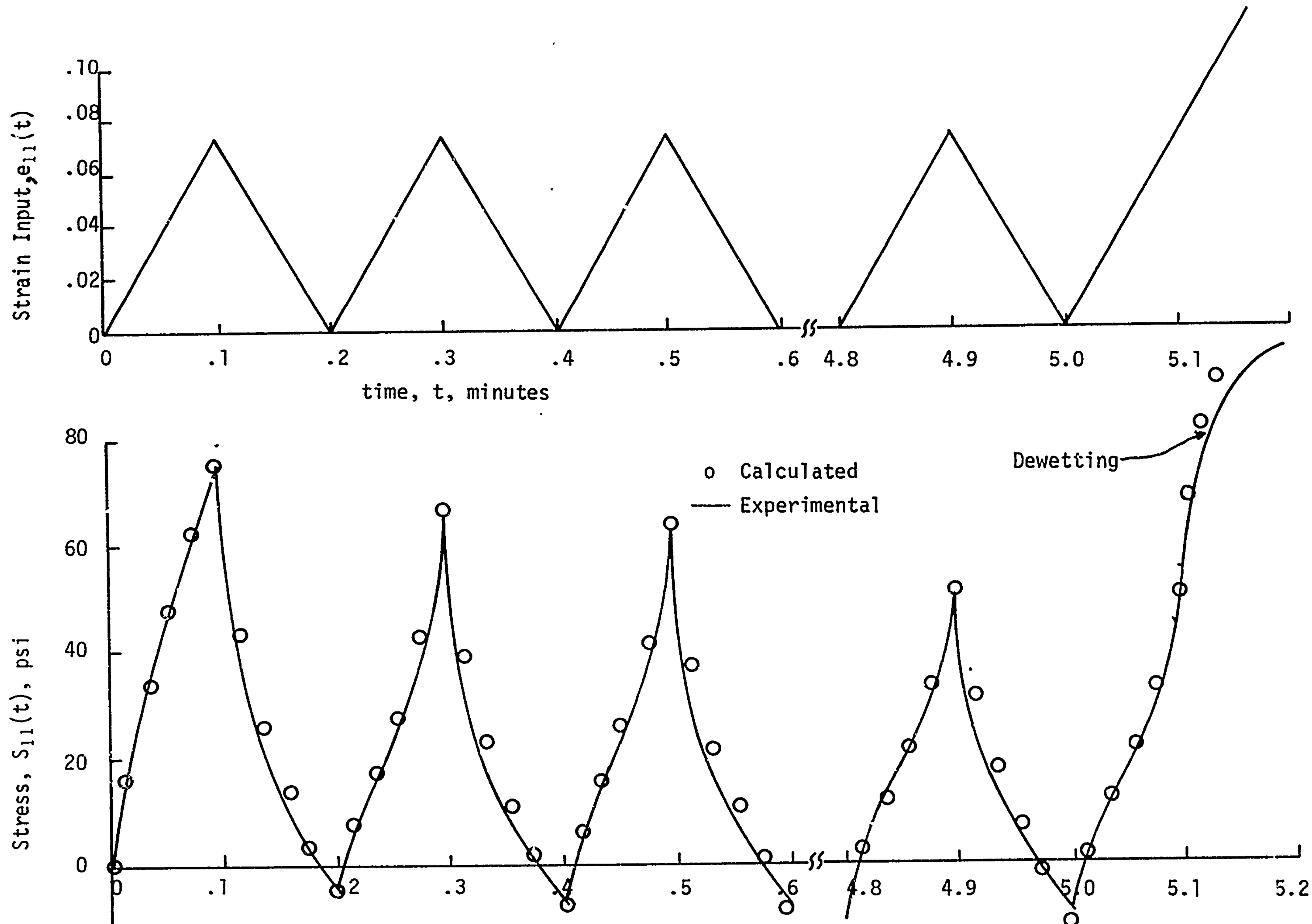


Figure 10.16. COMPARISON OF EXPERIMENTAL AND CALCULATED STRESS OUTPUT FOR A CYCLIC STRAIN INPUT.

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13. ABSTRACT

Nonlinear homogeneous constitutive equations are developed in this thesis for highly filled polymeric materials such as solid propellants. In the range of strains below vacuole dilatation these materials obey the homogeneity rule of linearity but do not obey the superposition rule. Such materials typically exhibit an irreversible "stress softening" called the "Mullins' Effect."

The development in this dissertation stems from attempting to mathematically describe the failing microstructure of these composite materials in terms of a linear cumulative damage model. It is demonstrated that p^{th} order Lebesgue norms of the strain history can be used to describe the state of damage in these materials and can also be used in the constitutive equation to characterize their time dependent mechanical response to strain disturbances.

Stress analysis procedures for materials having nonlinear homogeneous constitutive equations are developed for two and three dimensional proportional boundary value problems. A series of correspondence principles are derived wherein half of the solution, either the stresses or the strains, can be obtained by solving an equivalent linear elastic problem. The remaining half of the solution can be obtained by substituting the linear elastic solution into the nonlinear homogeneous constitutive equation.

The constitutive equation has been extended to include thermorheologically simple materials by defining a reduced time. It is also demonstrated that by using weighted p^{th} order Lebesgue norms the constitutive equation can also contain the rehealing of damage which is exhibited by highly filled polymeric materials.

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